VOL. LV, NO. 9, SEPTEMBER, 1960

THE Journal OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

PUBLISHED MONTHLY BY
THE AMERICAN LEATHER CHEMISTS ASSOCIATION
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The Journal

of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LV SEPTEMBER 1960 No. 9

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SUBSCRIPTION - - MEMBERS $12.00 A YEAR - - NONMEMBERS $15.00

Published Monthly by

The American Leather Chemists Association

Entered as Second-Class Matter at the Post Office, Easton, Pa.
Acceptance for mailing at special rate of postage as provided for in section 1103, Act of October 3, 1917, authorized July 16, 1918

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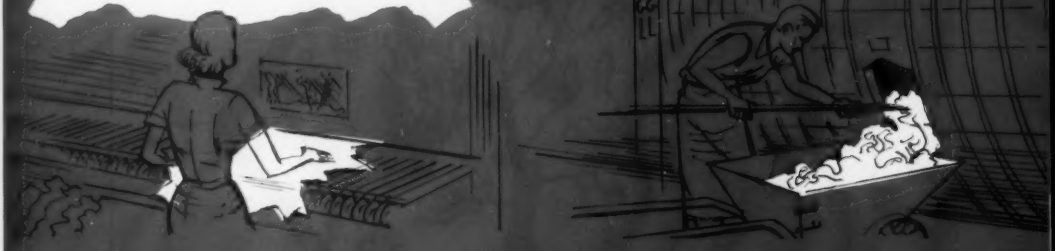

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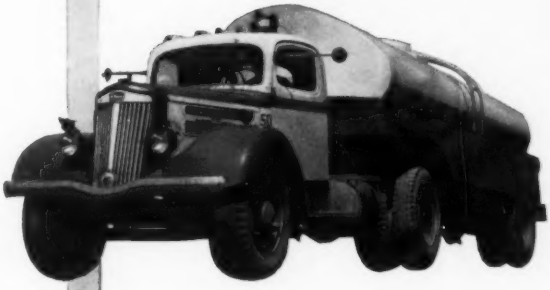

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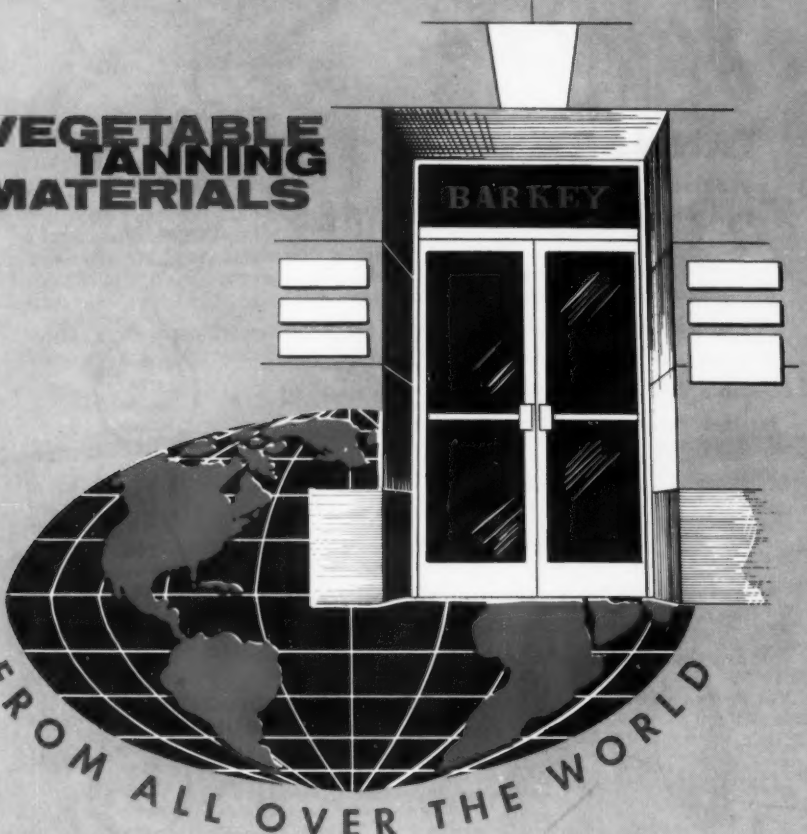

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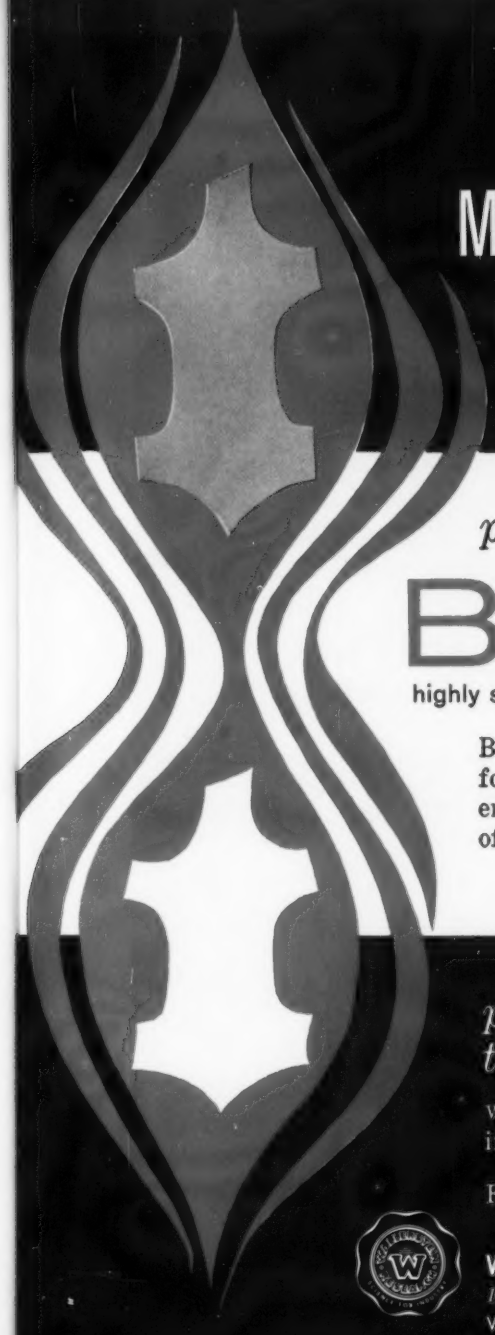

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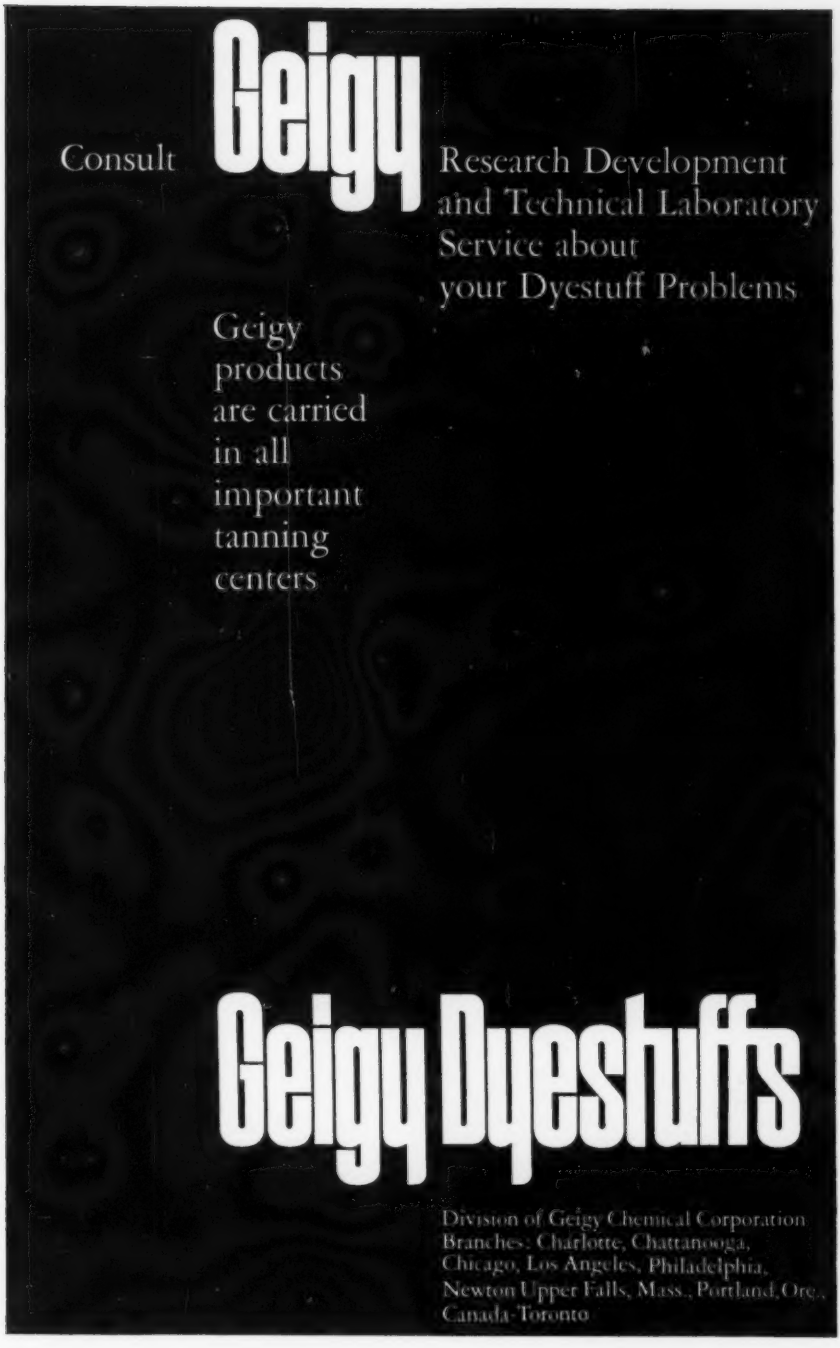
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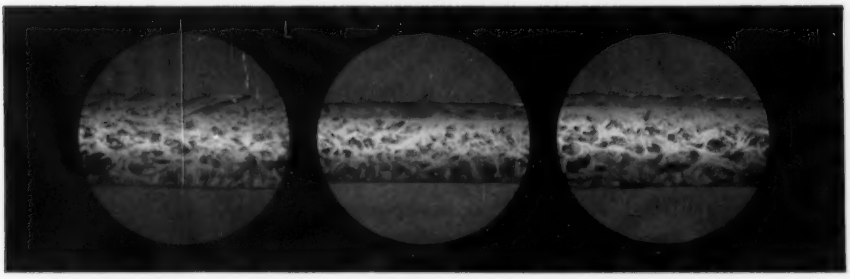

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Vol. LV SEPTEMBER 1960 No. 9

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General correspondence concerning the *Journal* should be mailed to the Managing Editor.
Subscriptions—$12 per year for members; $15 for nonmembers.

4-NITROPHENYL ESTERS, INCLUDING MIXED CARBONATES AND BIS CARBONATES, AS LEATHER FUNGICIDES*

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ABSTRACT

4-nitrophenyl derivatives lacking a free phenolic hydroxyl group have generally been neglected for serious consideration as leather fungicides in spite of the well known employment of the parent compound for this purpose. It has been assumed that among such derivatives a free hydroxyl group is essential for high fungitoxic potency. However, it has recently been shown that bis(4-nitrophenyl) carbonate and bis(2-chloro-4-nitrophenyl) carbonate in leather hydrolyze under mildew-growing conditions with liberation of the free nitrophenols. The two bis carbonates are approximately as effective as leather-mildew inhibitors as the phenols themselves. These findings prompted an investigation of additional esters of 4-nitrophenol and 2-chloro-4-nitrophenol. The results of this investigation are reported and discussed in the present paper. All these compounds behaved like the bis carbonates, i.e., they were all effective leather fungicides. Their potential advantages over 4-nitrophenol are discussed.

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INTRODUCTION

In a recent report the authors discussed various phases of the work on leather fungicides at the National Bureau of Standards (1). One finding discussed was that bis(4-nitrophenyl) carbonate and bis(2-chloro-4-nitrophenyl) carbonate are approximately as effective as leather-mildew pre-

*These studies were sponsored by the Quartermaster Corps of the Department of the Army as a part of research and development project 7-65-01-003B. This paper was presented at the Fifty-fifth Annual Meeting at Mackinac Island, Michigan, in 1959.

ventives as the corresponding free phenols, 4-nitrophenol and 2-chloro-4-nitrophenol. The latter two compounds are well known leather fungicides, 4-nitrophenol having been used for that purpose by the Quartermaster Corps since 1951. Earlier reports have emphasized the comparative scarcity of fungicides as effective as the above nitrophenols in preventing mildew growth on leather (2, 3).

Since it has been repeatedly observed that a free phenolic hydroxyl group is associated with high fungitoxic activity (1, 2, 4), it is presumed that the activity of the two bis carbonates mentioned above is due to hydrolysis under mildew-growing conditions, with liberation of the free nitrophenols. In support of this presumption, free nitrophenols could be detected in the leather specimens treated with the bis carbonates and tested for mildew resistance by exposure in a tropical room for five weeks. Complete hydrolysis could be demonstrated when the compounds were heated for ten minutes in sodium citrate solution.

It was thought that these compounds in the carbonate forms were probably nontoxic to fungi. Presumably, they are also less toxic to human skin than the phenols. This would be of practical value in their employment as leather fungicides, in that their concentration in the leather would not have to be carefully controlled (as is necessary with 4-nitrophenol). They are colorless and nearly insoluble in cold water, which are other attractive features. The bis carbonates, therefore, appear to have some substantial practical advantages over the 4-nitrophenols. This prompted the present investigation of additional hydrolyzable compounds of 4-nitrophenol and 2-chloro-4-nitrophenol. Eight esters, including four mixed carbonates, were synthesized for this purpose and were used in the present study together with the two bis carbonates.

MATERIALS

Table I shows the 4-nitrophenyl non-carbonate esters, mixed carbonates, and bis carbonates used in this investigation. The non-carbonate esters, (compounds 1 to 4) were prepared according to the method of Chattaway (5) from the appropriate phenol and acid anhydride. The mixed carbonates (compounds 5 to 8) were prepared according to the method of Ransom (6) from the appropriate phenol and chloroformate. The bis carbonates (compounds 9 and 10) were those used in the earlier investigation (1). They were purified by recrystallization from a toluene-ethanol mixture.

The 4-nitrophenol and 2-chloro-4-nitrophenol used in the above preparations and throughout this investigation and the acetic and propionic anhydride were "reagent grade." Ethyl and phenyl chloroformate were supplied as products at least 95% pure.

TABLE I

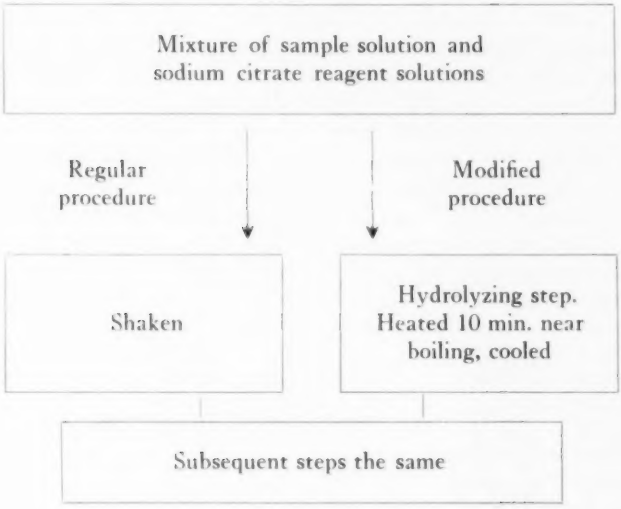
COMPOUNDS INVESTIGATED

No.	Name, Structure	Molecular Weight	M.P. °C.
1	4-nitrophenyl acetate $CH_3COOC_6H_4NO_2$	181.2	79–80
2	4-nitrophenyl propionate $C_2H_5COOC_6H_4NO_2$	195.2	61–62
3	4-nitrophenyl chloroacetate $CH_2ClCOOC_6H_4NO_2$	215.6	97–98
4	2-chloro-4-nitrophenyl chloroacetate $CH_2ClCOOC_6H_3ClNO_2$	250.1	79–80
5	ethyl 4-nitrophenyl carbonate $C_2H_5OCOOC_6H_4NO_2$	211.2	67–68
6	2-chloro-4-nitrophenyl ethyl carbonate $C_2H_5OCOOC_6H_3ClNO_2$	245.6	43–44
7	4-nitrophenyl phenyl carbonate $C_6H_5OCOOC_6H_4NO_2$	259.2	127–128
8	2-chloro-4-nitrophenyl phenyl carbonate $C_6H_5OCOOC_6H_3ClNO_2$	293.7	86–87
9	bis(4-nitrophenyl) carbonate $O_2NC_6H_4OCOOC_6H_4NO_2$	304.2	143–144
10	bis(2-chloro-4-nitrophenyl) carbonate $O_2NClC_6H_3OCOOC_6H_3ClNO_2$	373.1	160–161

Only two of the compounds listed in Table I have been reported in the literature. The melting point reported for 4-nitrophenyl acetate is 81°–82° C. (5), and that for ethyl 4-nitrophenyl carbonate is 67°–68° C. (6). Both values are in good agreement with those now observed for these compounds (Nos. 1 and 5).

EXPERIMENTAL PROCEDURES

Analytical procedures.—It has previously been shown (1) that the colorimetric procedure for 4-nitrophenol developed by Lollar (7) is also applicable to 2-chloro-4-nitrophenol and by a slight modification can be used for determination of hydrolyzable complexes of the two 4-nitrophenols. Thus, it has been used for determination of the two bis carbonates in leather (1). The modification consists of the insertion of a hydrolyzing step in the regular procedure, as shown by the following outline:


Mixture of sample solution and sodium citrate reagent solutions
Regular procedure
Modified procedure
Shaken
Hydrolyzing step. Heated 10 min. near boiling, cooled
Subsequent steps the same

The modified procedure was found to be applicable to all the compounds listed in Table I. Analysis by this procedure gave results that were in good agreement with the theoretical value (based on the structure shown in Table I and assuming 100% hydrolysis). This was considered satisfactory proof of structure and purity and also evidence of general applicability of the modified procedure for determination of the esterified 4-nitrophenols. The modified procedure measures total 4-nitrophenol content, i.e., esterified and free 4-nitrophenol. The regular procedure measures only free 4-nitrophenol. Reference to the "modified" and the "regular" analytical procedure will be made throughout this report.

Deposition of compounds in leather.—Specimens of a vegetable-crust sole leather were impregnated by immersion in solutions of the compounds. The solvent mixture consisted of 50% of *p*-dioxane, 10% of neatsfoot oil, and 40% of chloroform, by weight. Four concentrations were used.

The formulations used for deposition of the highest concentration-level were prepared first. Approximately equivalent concentrations, in terms of 4-nitrophenol or 2-chloro-4-nitrophenol liberated on complete hydrolysis, were prepared. The concentration aimed for was 10.8 milliequivalents per 100 grams of solution or 10.8 meq.%. The actual concentrations were determined by the modified analytical procedure and deviated somewhat from the 10.8 value. The values found by analysis (Table II, 1 day column) were used in computing the amounts of the compounds deposited in the leather specimens, based on the amounts of the solutions absorbed. The

TABLE II

ANALYSIS OF SOLUTIONS* PREPARED TO CONTAIN APPROXIMATELY 10.8 MILLIEQUIVALENTS (AS NITROPHENOL) PER 100 GRAMS OF SOLUTION (MEQ. %)

No.	Compound	Analysis of solution after 1 day A† meq. %	1 day B‡ meq. %	5 days A† meq. %	5 days B‡ meq. %	75 days A† meq. %	75 days B‡ meq. %
1	4-nitrophenyl acetate	11.7	0.0	11.4	0.0	12.6	0.0
2	4-nitrophenyl propionate	10.5	0.0	11.4	0.0	11.8	0.0
3	4-nitrophenyl chloroacetate	11.7	0.0	12.1	0.0	12.6	0.7
4	2-chloro-4-nitrophenyl chloroacetate	10.7	0.0	11.0	0.0	12.7	1.1
5	ethyl 4-nitrophenyl carbonate	10.4	0.0	10.4	0.0	11.8	0.0
6	2-chloro-4-nitrophenyl ethyl carbonate	9.7	0.0	9.7	0.0	10.6	0.0
7	4-nitrophenyl phenyl carbonate	11.3	0.0	11.0	0.0	11.8	0.0
8	2-chloro-4-nitrophenyl phenyl carbonate	9.5	0.0	10.3	0.0	——	——
9	bis(4-nitrophenyl) carbonate	11.9	0.0	11.9	0.0	12.9	0.8
10	bis(2-chloro-4-nitrophenyl) carbonate	10.7	0.0	10.3	0.0	11.7	0.8
—	4-nitrophenol	11.5	11.5	11.6	11.8	12.9	12.9
—	2-chloro-4-nitrophenol	11.0	11.0	10.9	10.5	11.7	11.7

*Solvent: 50% of *p*-dioxane, 10% of neatsfoot oil, 40% of chloroform. Aliquots used for analysis were diluted with chloroform so that final chloroform content was at least 96%.
†A = Modified analytical procedure (esterified + free nitrophenol).
‡B = Regular analytical procedure (free nitrophenol only).

solutions used for impregnation of leather specimens with the three lower concentrations were prepared by successive 1:1 dilutions of the original solution, using the same solvent mixture.

Four leather specimens were impregnated at each concentration level. Two of these specimens were stored in the laboratory, and two were used for determination of mildew resistance.

Test for fungitoxic potency

In leather.—The leather specimens were tested for mildew resistance by exposure for eight weeks in the tropical room at the U. S. Army Engineering Center at Fort Belvoir, Virginia (1). The amount of mildew growth on the

leather was estimated visually during weekly inspections. Very little additional growth occurred after five to six weeks. The amount of growth after eight weeks was used as a measure of mildew resistance. Five categories of mildew resistance were used, depending on the percentages of the total surface area covered (3). Since untreated specimens (controls) exposed simultaneously were completely covered with mildew, the categories above could be converted into corresponding ones expressed in terms of percent inhibition of mildew growth (Fig. 1).

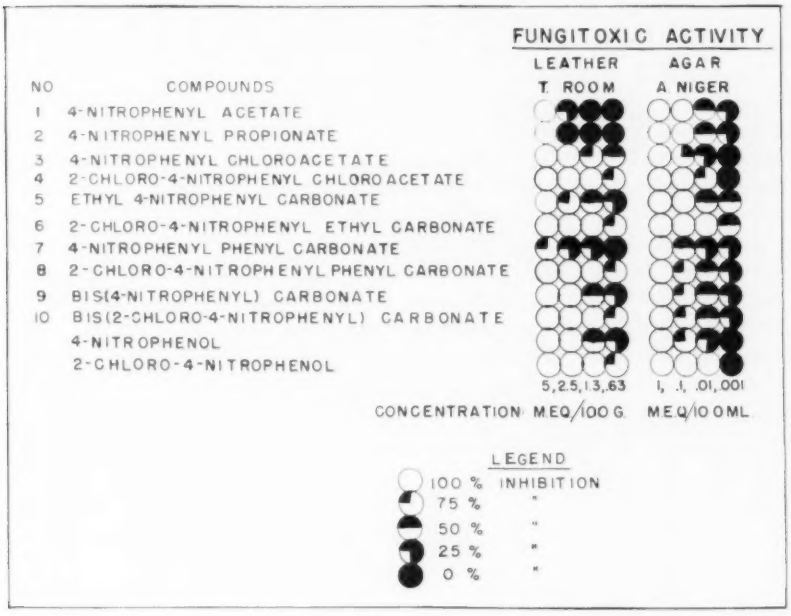


FIGURE 1.

In nutrient agar.—This test was performed at the Quartermaster laboratories using the agar petri dish technique (8). The fungitoxic potency was expressed as the percent inhibition of growth of *A. niger* on agar plates containing certain concentrations of the fungicides (as compared to the growth on agar not containing fungicides). The concentrations used were 1, 0.1, 0.01, and 0.001 milliequivalents, as nitrophenol, per 100 ml. of agar.

HYDROLYTIC STABILITY OF THE FUNGICIDES IN SOLUTION

The solutions used in treating leather specimens were tested for total fungicide concentration and for free nitrophenols by the modified and regular

TABLE III

EFFECT OF SOLVENT COMPOSITION ON HYDROLYTIC STABILITY OF FUNGICIDES

Solvent mixture (by volume): p-dioxane and chloroform in the ratios $\frac{p\text{-dioxane}}{chloroform}$ *indicated*

No.	Compound	R =	% Hydrolysis* of fungicide							
			0/100	4/96	20/80	44/56	64/36	84/16	92/8	96/4	100/0
1	4-nitrophenyl acetate		0	0	0	6.8	10.8	27.0	59.5	97.3	100.0
2	4-nitrophenyl propionate		0	0	0	0	5.4	13.5	37.8	81.1	100.0
3	4-nitrophenyl chloroacetate		0	0	9.1	10.4	13.0	36.4	57.1	93.5	98.7
4	2-chloro-4-nitrophenyl chloroacetate		0	0	7.5	10.4	10.4	17.9	47.8	95.5	98.5
5	ethyl 4-nitrophenyl carbonate		0	0	0	0	0	9.5	17.6	89.2	100.0
6	2-chloro-4-nitrophenyl ethyl carbonate		0	0	0	0	0	12.1	25.8	84.8	100.0
7	4-nitrophenyl phenyl carbonate		0	0	0	5.4	5.4	8.1	18.9	45.9	100.0
8	2-chloro-4-nitrophenyl phenyl carbonate		0	0	0	7.6	7.6	10.6	15.2	66.7	100.0
9	bis(4-nitrophenyl) carbonate		0	0	0	6.1	7.3	14.6	36.6	48.8	90.2
10	bis(2-chloro-4-nitrophenyl) carbonate		0	0	0	6.8	8.1	13.5	32.4	43.2	83.8

*$\%$ hydrolysis $= \frac{100\ B}{A}$ where

B = meq. % (as the nitrophenol) found by regular procedure.
A = meq. % (as the nitrophenol) found by modified procedure.
Whenever B, due to experimental error, was larger than A, % hydrolysis was taken to be 100.0.

analytical procedures at 1, 5, and 75 days after preparation. The results (Table II) show that there was no evidence of decomposition of the non-carbonate esters, mixed carbonates, or bis carbonates after standing 5 days. However, after 75 days there was slight (up to 10%) decomposition of the bis carbonates and chloroacetates of both nitrophenols. (Evaporation of solvents from the screw-top bottles in which the solutions were kept is thought to be the cause of the gradual increase in fungicide content apparent from Table II).

The effect of solvent composition on hydrolytic stability was investigated. Stock solutions of the fungicides in *p*-dioxane (0.01 *M* conc.) were diluted with various solvents (ethanol, chloroform, and trichloroethylene), and the solvent mixture was used for treatment of leathers (Table II, footnote *a*). Aliquots of the diluted solutions containing 0.0008 meq. of the fungicides (as nitrophenol) were tested for free nitrophenol by the regular analytical procedure. It was found that when the solvent mixture in the sample aliquot consisted of at least 96% (by volume) of a water-immiscible solvent (chloroform or trichloroethylene), no hydrolysis occurred, i.e., no free nitrophenol was found. If the solvent mixture contained only water-miscible solvents (*p*-dioxane or ethanol), virtually complete hydrolysis occurred. These results were obtained whether the solutions were freshly prepared or several days old. These results indicate that the non-carbonate esters, mixed carbonates, and bis carbonates are hydrolyzed by the aqueous sodium citrate reagent used in the analytical procedure if they are allowed to come into contact with it, but are stable in the water-immiscible solvents. Presumably, in the latter case, the test compound remains entirely in the organic solvent phase.

TABLE IV

RATE OF HYDROLYSIS IN 70% (VOL.) AQUEOUS *p*-DIOXANE BUFFERED AT pH 3 AT 40° C.

No.	Compound	K, Min^{-1}	Relative Rate
1	4-nitrophenyl acetate	4.33×10^{-6}	1
2	4-nitrophenyl propionate	3.75×10^{-6}	0.9
3	4-nitrophenyl chloroacetate	1.29×10^{-3}	298
4	2-chloro-4-nitrophenyl chloroacetate	3.82×10^{-3}	882
5	ethyl 4-nitrophenyl carbonate	2.88×10^{-6}	0.7
6	2-chloro-4-nitrophenyl ethyl carbonate	1.53×10^{-5}	3.5
7	4-nitrophenyl phenyl carbonate	1.71×10^{-4}	40
8	2-chloro-4-nitrophenyl phenyl carbonate	3.57×10^{-4}	82
9	bis(4-nitrophenyl) carbonate	8.82×10^{-3}	2037
10	bis(2-chloro-4-nitrophenyl) carbonate	3.24×10^{-2}	7483

The effects of mixtures of *p*-dioxane (water-miscible) and chloroform (water-immiscible), varying from 100% of one solvent to 100% of the other, on hydrolytic stability of the fungicides are shown in Table III. The results show that all the compounds are stable in *p*-dixoane stock solutions and that hydrolysis does not occur during analysis if the solvents of the sample solution consist of at least 96% chloroform.

Taking advantage of these facts, it has been possible to measure the rate of hydrolysis of these compounds in aqueous *p*-dioxane solutions. The results that have been obtained in 70% (by volume) aqueous *p*-dioxane solutions buffered at pH 3, at 40° C. are given in Table IV. Under the experimental conditions used, the rate of hydrolysis was first-order. The specific rate-constants are shown, as well as the *relative* rates (taking that of 4-nitrophenyl acetate as 1). It may be seen that there is a 7000-fold range in the rates of hydrolysis of these compounds.

FUNGITOXIC ACTIVITY

The results of the mildew-resistance test of treated leather exposed in the tropical room and the inhibition of *A. niger* on treated agar are shown graphically in Fig. 1. The four concentrations in leather are shown in rounded values. It is clear that all the compounds exhibited fungitoxic activity. In only one case (compound 7) did the highest concentration (5 meq 100 g) completely fail to prevent mildew on leather. The highest concentration used in agar (1 meq 100 ml) produced 100% inhibition of *A. niger* in all cases.

As is often observed with different substrates, there are different responses among the compounds in the two tests. Thus, the acetic and the propionic acid esters of 4-nitrophenol (compounds 1 and 2) appeared to be relatively less effective in leather than in agar. In leather these compounds were much less effective than the chloroacetic acid esters (compounds 3 and 4), whereas in agar there was not much difference. The higher potency of 2-chloro-4-nitrophenol derivatives (Nos. 4, 6, 8, and 10) compared to the corresponding 4-nitrophenol derivatives (Nos. 3, 5, 7, and 9) is very pronounced in leather and less so in agar. The differences among the derivatives in leather are similar to the difference between the corresponding free phenols listed last in Fig. 1.

The general fungitoxic activity exhibited by this group of compounds indicates a common fungitoxic substance and a common mode of action. It is hardly possible that the fungitoxic substance could be anything but the free nitrophenol liberated on hydrolysis. If hydrolysis is required for fungitoxic activity, one would expect activity to decrease with increasing hydrolytic stability. Compounds reaching or exceeding a certain level of stability could be expected to have no activity. If this is correct, that level

of stability was apparently not reached by *any* of the esters used in this investigation. However, it may be significant that compounds 1, 2, and 7, which exhibited comparatively low activity in leather, were also hydrolyzed comparatively slowly in aqueous *p*-dioxane solution. On the other hand, compounds 5 and 6 were hydrolyzed even more slowly than compound 7, and yet they exhibited higher fungitoxic potency. The explanation for this is not apparent. Perhaps the rate of hydrolysis in aqueous *p*-dioxane does not always correctly indicate the rate actually operative in leather. It has been shown that hydrolysis of 4-nitrophenyl acetate is catalyzed by imidazole (9, 10). The imidazole ring is present in histidine. Histidine or similar materials in leather may produce hydrolysis rates different from those shown in Table IV.

Shirk and Gertler have recently shown that fungitoxic activity is a general property of alcoholic esters of bromoacetic acid (11). Phenolic esters were not investigated. Many of the bromoacetic acid esters were more fungitoxic than bromoacetic acid itself. These investigators discuss the possibility that a common fungitoxic agent of all the esters may be liberated by esterase action after permeation of the cell wall of the organism. The esters, because of their lipophilic nature, may be more able to penetrate the cell wall and hence exhibit greater activity than the free acid.

There is no evidence for hydrolysis of the compounds used in this investigation within cells, although this may be their mode of action. Proof of this would be important in their application as leather fungicides It would mean that the organism itself is the converter of the original ester to a fungitoxicant. This would constitute a more positive regulatory system than hydrolysis in response to heat and moisture, i.e., mildew-growing conditions, as has been postulated (1).

STABILITY OF FUNGICIDES IN LEATHER

The set of leather specimens exposed in the tropical room had a companion set that was stored in the laboratory. The specimens containing the highest concentration level of fungicide were analyzed for fungicide content five months after treatment. The results are presented in Tables V, VI, and VII.

Loss by heating for 16 hours at 100° C.— From column A, Table VI, it may be seen that heating for 16 hours at 100° C. generally caused only small losses of fungicides from the samples with prior exposure in the tropical room (T.R.). The losses from the samples heated after storage in the laboratory (lab.) for five months were generally higher, being appreciable especially for the carbonates (compounds 5, 6, 7, 8, and 10), and reaching approximately 30% for the 2-chloro-4-nitrophenyl ethyl carbonate (No. 6). The observation that higher losses occurred from "lab." samples than from "T.R."

TABLE V

FUNGICIDE CONTENT OF LEATHER SAMPLES AFTER 5 MONTHS*

No.	Fungicide	Sample set	Moisture† %	Anal.‡ Method	Fungicide content: Specimens dried at 100° C for 16 hr.** No water added meq. %	Specimens dried at 100° C for 16 hr.** 2 ml. water added†† meq. %	Specimens not dried No water added meq. %	Specimens not dried 2 ml. water added meq. %
1	4-nitrophenyl acetate	Lab.	10.2	A	0.44	4.18	4.12	4.28
				B	0.27	2.20	1.61	1.70
		T.R.	10.9	A	0.32	2.20	1.98	2.20
				B	0.24	2.09	1.89	2.16
2	4-nitrophenyl propionate	Lab.	9.9	A	0.44	3.28	3.38	3.60
				B	0.20	1.35	0.89	1.12
		T.R.	11.1	A	0.31	2.02	1.91	2.04
				B	0.29	2.00	1.85	2.00
3	4-nitrophenyl chloroacetate	Lab.	10.2	A	0.36	5.26	4.96	5.25
				B	0.36	5.12	4.90	5.22
		T.R.	11.0	A	0.60	5.16	5.08	5.26
				B	0.60	5.10	4.98	5.30
4	2-chloro-4-nitrophenyl chloroacetate	Lab.	9.6	A	0.38	5.11	5.09	5.28
				B	0.38	4.93	4.64	4.98
		T.R.	11.0	A	0.25	3.13	2.61	3.22
				B	0.25	3.15	2.48	3.22
5	ethyl 4-nitrophenyl carbonate	Lab.	10.3	A	0.47	2.86	3.47	3.68
				B	0.14	0.63	0.27	0.27
		T.R.	11.0	A	0.36	2.38	2.38	2.61
				B	0.29	2.00	1.58	1.71
6	2-chloro-4-nitrophenyl ethyl carbonate	Lab.	10.5	A	0.89	2.59	3.51	3.69
				B	0.28	0.95	0.38	0.38
		T.R.	11.1	A	0.36	2.54	2.16	2.56
				B	0.34	2.36	1.71	2.02
7	4-nitrophenyl phenyl carbonate	Lab.	10.5	A	2.91	4.47	5.36	5.32
				B	0.47	1.36	0.50	0.54
		T.R.	11.4	A	0.70	3.66	3.84	3.95
				B	0.63	3.54	3.16	3.32
8	2-chloro-4-nitrophenyl phenyl carbonate	Lab.	9.9	A	1.95	2.80	3.62	3.60
				B	0.44	1.18	0.76	0.80
		T.R.	10.8	A	0.68	5.34	4.93	5.29
				B	0.68	5.25	4.66	5.24

TABLE V—*Continued*

No.	Fungicide	Sample set	Moisture† %	Anal.‡ Method	Fungicide content: Specimens dried at 100° C for 16 hr.** No water added meq. %	Specimens dried at 100° C for 16 hr.** 2 ml. water added†† meq. %	Specimens not dried No water added meq. %	Specimens not dried 2 ml. water added meq. %
9	bis(4-nitrophenyl) carbonate	Lab.	10.3	A	2.05	5.48	5.76	5.68
				B	0.87	3.99	2.83	3.08
		T.R.	10.8	A	0.83	5.58	5.42	5.70
				B	0.77	5.54	5.36	5.58
10	bis(2-chloro-4-nitrophenyl) carbonate	Lab.	10.5	A	1.61	4.09	4.87	5.05
			10.7	B	0.92	3.24	2.32	2.59
		T.R.		A	0.58	3.96	3.94	4.12
				B	0.50	3.88	3.76	4.00
11	4-nitrophenol	Lab.	10.4	A	0.45	5.29	4.90	5.28
				B	0.45	5.29	4.90	5.28
		T.R.	11.0	A	0.61	5.08	4.90	5.20
				B	0.61	5.08	4.90	5.20
12	2-chloro-4-nitrophenol	Lab.	10.0	A	0.42	4.75	4.60	4.93
				B	0.42	4.75	4.60	4.93
		T.R.	11.1	A	0.38	3.02	2.84	3.13
				B	0.38	3.02	2.84	3.13

*One set of samples (Lab.) was stored in the laboratory for the entire 5 months. A duplicate set (T.R.) was exposed in the tropical room at Fort Belvoir for 2 months and in the laboratory for the remaining 3 months. Each sample, which consisted of two 2" x 4" leather specimens, was ground in a Wiley mill, mixed, reconditioned for 2 weeks at 24°C. and 50% relative humidity, and kept in closed containers. 2.5 -g. specimens were used for analysis. The values in the table are given as milliequivalents of the free nitrophenol per 100 g. of moisture-free leather (meq. %). Each value is the average of two determinations.

†From weight lost by heating at 100° C. for 16 hours. The percentage shown is the average of two determinations.

‡A = modified analytical procedure (esterified + free nitrophenols).
B = regular analytical procedure (free nitrophenols only).

**After moisture determination, the specimen was immediately transferred to the extraction thimble and extracted with chloroform. After 2.5 hours extraction the specimen was squeezed free of most of the chloroform and left in the thimble overnight. 2 ml. of water was then added and extraction repeated. The value given in the table for the second extraction (2 ml. of water added) includes that obtained on the first extraction and consequently must always be the higher. The same procedure was followed with the specimens not dried, except that in some cases separate specimens were used for the two extractions. When separate specimens were used with approximately equal amounts of fungicide extracted, the amount found in the specimen with water added could be the lower. The values for compounds 7, 8, and 9, lab. samples, were obtained in this way.

††A third extraction, after further addition of 2 ml. of water, failed to extract more fungicide from any specimen, showing that removal was complete after the second extraction.

TABLE VI

STABILITY OF FUNGICIDES IN LEATHER, CALCULATED FROM THE RESULTS GIVEN IN TABLE V

The values in all cases are percentages of total fungicide content found in the respective specimens.

No.	Fungicide	Sample set	Fungicide lost by heating 16 hr. at 100°C. %*	Fungicide retained by dry leather† %	Unhydrolyzed fungicide in extracts‡, %				Fungicide lost by exp. for 2 mo. in T.R.** %
					Spec. dried at 100°C.		Spec. not dried		
					No water	Water added	No water	Water added	
			A	B	C	D	E	F	G
1	4-nitrophenyl acetate	Lab.	2.3	89.5	38.6	47.4	60.9	60.3	48.6
		T.R.	0.0	85.5	25.0††	5.0	4.5	1.8	
2	4-nitrophenyl propionate	Lab.	8.9	86.6	54.5	58.8	73.7	68.9	43.3
		T.R.	1.0	84.7	6.5	1.0	3.1	2.0	
3	4-nitrophenyl chloroacetate	Lab.	0.0	93.1	0.0	2.7	1.2	0.6	0.0
		T.R.	1.9	88.4	0.0	1.2	2.0	0.0	
4	2-chloro-4-nitrophenyl chloroacetate	Lab.	3.2	92.6	0.0	3.5	8.8	5.7	39.0
		T.R.	2.8	92.0	0.0	0.0	5.0	0.0	
5	ethyl 4-nitrophenyl carbonate	Lab	22.3	83.6	70.2	78.0	92.2	92.7	29.1
		T.R.	8.8	84.9	19.4	16.0	33.6	34.5	
6	2-chloro-4-nitrophenyl ethyl carbonate	Lab.	29.8	65.6	68.5	63.3	89.2	89.7	30.6
		T.R.	0.8	85.8	5.6	7.1	20.8	21.1	
7	4-nitrophenyl phenyl carbonate	Lab.	16.0	34.9	83.8	69.6	90.7	89.8	25.8
		T.R.	7.3	80.9	10.0	3.3	17.7	15.9	
8	2-chloro-4-nitrophenyl phenyl carbonate	Lab.	22.2	30.4	77.4	57.9	79.0	77.8	
		T.R.	0.0	87.3	0.0	1.7	5.5	0.9	‡‡
9	bis(4-nitrophenyl) carbonate	Lab.	3.5	62.6	57.6	27.2	50.9	45.8	0.0
		T.R.	3.0	85.0	7.2	0.0	1.1	2.1	

10	bis(2-chloro-4-nitrophenyl) carbonate	Lab.	19.0	60.6	42.9	20.8	52.4	48.7	18.4
		T.R.	3.9	85.4	13.8	2.0	4.6	2.9	
11	4-nitrophenol	Lab.	0.0	91.5	—	—	—	—	1.5
		T.R.	2.3	88.0	—	—	—	—	
12	2-chloro-4-nitrophenol	Lab.	3.7	91.0	—	—	—	—	36.5
		T.R.	3.5	86.9	—	—	—	—	

*Fungicide loss by heating 16 hr. at 100°C., $\% = \frac{(a-b)}{a} \times 100$ where (from Table V) a = meq. % found in specimens not dried, water added, modified analytical procedure used, and b = meq. % found in specimen dried, water added, modified analytical procedure used.

Example: Fungicide No. 1, Lab., $\frac{(4.28 - 4.18)}{4.28} \times 100 = 2.3$

†Fungicide retained by dry leather, $\% = \frac{(a-b)}{a} \times 100$ where (from Table V) a = meq. % found in specimens dried, water added, modified analytical procedure used, and b = meq. % found in specimens dried, no water added, modified analytical procedure used.

Example: Fungicide No. 1, Lab., $\frac{(4.18 - 0.44)}{4.18} \times 100 = 89.5$

‡Fungicide unhydrolyzed, $\% = \frac{(a-b)}{a} \times 100$ where (from Table V) a = meq. % found when the modified analytical procedure was used, and b = meq. % when the regular analytical procedure was used, and a and b were obtained on the same extract.

Example: Fungicide No. 1, Lab., column C, $\frac{(0.44 - 0.27)}{0.44} \times 100 = 38.6$

**Fungicide loss by exposure for 2 months in tropical room, $\% = \frac{(a-b)}{a} \times 100$ where (from Table V) a = meq. % found in specimens not dried, lab. set of samples, modified analytical procedure used, and b = meq. % found in specimens not dried, T.R. set of samples.

Example: Fungicide No. 1, $\frac{(4.28 - 2.20)}{4.28} \times 100 = 48.6$

††The analytical values, from Table V, used to calculate the percentages in column C were quite small. Therefore, within the precision of the analytical method an error in the experimental values would have a large effect on the calculated percentages. This probably accounts for the unusually high percentage (25) shown for fungicide No. 1, T.R. sample, in column C compared to the corresponding percentages shown in columns D, E, and F (5 or less).

‡‡In the case of 2-chloro-4-nitrophenyl phenyl carbonate (No. 8), a considerably higher fungicide content was found in the T.R. sample than in the Lab. sample. The meq. percentages were 5.29 and 3.60, respectively (last column, Table V). This erratic result was found to be due to the loss of fungicide from the lab. sample as follows: The lab. sample, before grinding, had a heavy "bloom" or white, surface deposit. When tested, this bloom was found to contain fungicide. During the grinding operation, much of this deposit was undoubtedly lost. Neither the companion T.R. sample nor any of the other samples showed any bloom. The high proportion of fungicide found in the the T.R. sample, compared with that calculated from the treatment (4.59 meq., Table VII), indicates little or no loss of 2-chloro-4-nitrophenyl phenyl carbonate. However, since it could not be calculated from the analytical data, no result is reported for this fungicide in the last column of Table V. The fact that 2-chloro-4-nitrophenyl phenyl carbonate migrated to the surface of the lab. sample and did not do so in the case of the T.R. sample must be associated with differences in the two storage conditions. This, again, may be a case of redistribution and better fixation of the fungicide in the T.R. sample by the mechanisms that have been discussed on p. 494.

TABLE VII

APPARENT LOSS OF FUNGICIDE BY STORAGE FOR 5 MONTHS IN THE LABORATORY

No	Fungicide	Fungicide concentration in leather		
		Original (calc.)* meq. %	Found† after 5 mo. meq. %	Apparent loss‡ %
1	4-nitrophenyl acetate	5.65	4.28	24.2
2	4-nitrophenyl propionate	5.06	3.60	28.9
3	4-nitrophenyl chloroacetate	5.63	5.25	6.7
4	2-chloro-4-nitrophenyl chloroacetate	5.02	5.28	−5.2
5	ethyl 4-nitrophenyl carbonate	5.03	3.68	26.8
6	2-chloro-4-nitrophenyl ethyl carbonate	4.69	3.69	21.3
7	4-nitrophenyl phenyl carbonate	5.46	5.32	2.6
8	2-chloro-4-nitrophenyl phenyl carbonate	4.59	3.60	21.6
9	bis(4-nitrophenyl) carbonate	5.75	5.68	1.2
10	bis(2-chloro-4-nitrophenyl) carbonate	5.17	5.05	2.3
11	4-nitrophenol	5.57	5.28	5.2
12	2-chloro-4-nitrophenol	5.28	4.93	6.6

*Calculated from the amount of solution that was absorbed by the leather and the fungicide concentration in the solution. Nonpreferential absorption of solution components was assumed.

†From Table V, specimens not dried, lab. set of samples, water added, modified analytical procedure used.

‡Calculated as follows: $\frac{(\text{Original } \% - \text{found } \%) \times 100}{\text{Original } \%}$

samples by heating was surprising. Possibly the exposure in the tropical room causes redistribution of the fungicides from the original deposition on the exterior of the fibers. Softening of the fibers by absorption of moisture from the humid atmosphere in the tropical room may permit easier penetration of the fungicides to interior portions. In this way two types of fixation of the fungicide may occur: (*a*) chemical bonding with reactive groups in the leather and (*b*) physical enclosure in the fibers on subsequent drying. Both types of fixation could probably prevent loss arising from dry-heat volatilization.

Retention by dry leather.—Column B, Table VI, shows the percentage of the fungicides that failed to be extracted by chloroform from the specimens that had been dried to 0 % moisture. Regaining of moisture during the transfer of the specimens to the extraction thimbles undoubtedly occurred and was probably not the same for different specimens. Since small variations in moisture regain probably influenced the results appreciably, not too much

significance can be attached to such differences among the various fungicides. However, it is clear that with all these fungicides large proportions failed to be extracted from the dry leather. This behavior was previously encountered with 4-nitrophenol (12), and the fixation was ascribed to hydrogen bonding, involving the hydroxyl group (1). Since this group is not present in the esters, the implication is that both esterified and free nitrophenols are fixed physically rather than chemically.

Hydrolytic stability.—The percentages of the esters that remained unhydrolyzed in the four extracts are given in columns C to F of Table VI.

The results show that heating at 100° C. for 16 hours had less hydrolytic effect than exposure for two months in the tropical room. For example, the unhydrolyzed portion of 4-nitrophenyl acetate (No. 1) in the extract from the Lab. sample, not dried, water added, was found to be 60.3% (column F). The corresponding value for the sample that had been heated was 47.4% (column D), while for the sample exposed in the tropical room it was 1.8% (column F, T. R.). Similar results were obtained with the other fungicides. In some cases, for example, with fungicides 8, 9, and 10, addition of water to the dried specimens appeared to have an appreciable hydrolytic effect, i.e., about 20–30% reduction of unhydrolyzed material occurred.

The highest percentages of unhydrolyzed fungicides in leather *not* exposed in the tropical room or dried at 100° C. were found with the ethyl and phenyl mixed carbonates (compounds 5, 6, 7, and 8; 80–90% unhydrolyzed). These compounds appeared to be the most stable in leather under normal laboratory conditions. Esters 1 and 2 (60–70% unhydrolyzed) were next, then the bis carbonates (compounds 9 and 10; 40–50% unhydrolyzed), and finally, the chloroacetates (compounds 3 and 4), which were almost completely hydrolyzed. When the leather had been exposed for two months in the tropical room, all the compounds were almost completely hydrolyzed except some of the 4-nitrophenyl carbonates. The compound most resistant to hydrolysis was ethyl 4-nitrophenyl carbonate (No. 5).

These relative stabilities in leather agree, in part, with the indications given by the rates of hydrolysis in aqueous *p*-dioxane solution at pH 3 (Table IV). Thus, the bis carbonates and chloroacetates were hydrolyzed fastest in *p*-dioxane solution and therefore could be expected to be hydrolyzed most extensively in leather, as they were. However, in *p*-dioxane solution the bis carbonates were hydrolyzed about ten times as fast as the chloroacetates, but they were more stable in leather.

Similarly, among the ethyl and phenyl mixed carbonates (compounds 5, 6, 7, and 8) the percentages of unhydrolyzed compound in leather are in the order indicated by the hydrolysis rates in *p*-dioxane solution. However, these carbonates appeared to be more resistant to hydrolysis in leather than

esters 1 and 2, although the latter compounds had relatively low hydrolysis rates in *p*-dioxane solution.

Hydrolysis occurred with only two of the fungicides on boiling with chloroform (as in the extraction procedure). The extent of hydrolysis found for the two chloroacetates (compounds 3 and 4) was 5% and 8%, respectively, which is negligible compared to the 90–100% hydrolysis observed in the leather extracts.

Loss of fungicide during exposure for two months in the tropical room.—The last column in Table VI shows the fungicide losses attributable to exposure for two months in the tropical room. The losses of the fungicides varied from 0% to nearly 50%. This problem has been investigated before for some fungicides, including 4-nitrophenol and 2-chloro-4-nitrophenol (1).

The results for the two free nitrophenols in the present study agree quite well with those obtained earlier, i.e., 2-chloro-4-nitrophenol is more susceptible to loss than is 4-nitrophenol. The compounds that are easily hydrolyzed could be expected to behave similarly to the free nitrophenols, since the latter compounds would be present after hydrolysis . There is very good agreement with this postulate in the results obtained with the two chloroacetates, which are the most easily hydrolyzed. The loss of 2-chloro-4-nitrophenyl chloroacetate was 39.0%, corresponding to 36.5% for 2-chloro-4-nitrophenol, and the loss of 4-nitrophenyl chloroacetate was 0.0%, corresponding to 1.5% for 4-nitrophenol. Similarly, bis(2-chloro-4-nitrophenyl) carbonate showed a higher loss than bis(4-nitrophenyl) carbonate, 18.4% and 0.0%, respectively. With esters that are only partially hydrolyzed, the loss will, of course, depend to a greater degree on the susceptibility to loss of the unhydrolyzed portion. Volatilization is probably involved in these losses (1).

Apparent loss of fungicides during laboratory storage.—The calculated amounts of fungicides deposited in the leather at the time of treatment are compared in Table VII with the amounts found five months later by analyses of the specimens that had been stored in the laboratory. The analytical values for all fungicides except No. 4 are smaller than those calculated, thus indicating loss of fungicide during the time interval. The last column gives the losses in percentages based on the calculated values.

In the calculated values nonpreferential absorption of solution components was assumed in all cases. This assumption may not be valid for all of the compounds, although in previous investigations as in this one calculated and analytical values for 4-nitrophenol are in good agreement. Since in the present investigation the samples were not analyzed immediately after treatment, there is some question as to whether or not the losses for fungicides 1, 2, 5, and 6 are real. The increase of fungicide content with No. 4 is attributed to experimental error. In the case of fungicide No. 8, surface deposition with consequent rubbing off during handling and grinding of the

specimens was evidently a major factor contributing to the low "found" value (footnote 6, Table VI). With fungicides 3, 4, 7, 9, 10, 11, and 12 there is good agreement between the calculated and found values.

SUMMARY

All the compounds investigated exhibited fungitoxic activity, thus indicating a common fungitoxic substance. This substance is the free nitrophenol liberated by hydrolysis.

The rates of hydrolysis of the compounds in aqueous *p*-dioxane at pH 3 and 40° C. varied 7000-fold. However, the variations in effectiveness as leather fungicides were not great. At a concentration of 5 milliequivalents (as nitrophenol) per 100 grams of leather, nine of the ten compounds produced 100% inhibition of mildew on leather exposed in a tropical room. Derivatives of 2-chloro-4-nitrophenol were more potent than those of 4-nitrophenol, corresponding exactly to the difference in potency between the parent compounds. Even though 2-chloro-4-nitrophenol appears to be more susceptible to loss (from leather, during exposure to mildew-growing conditions), it prevents mildew at lower dosages, at least temporarily.

The non-carbonate esters and mixed carbonates, like the bis carbonates (1), are colorless, less water-soluble than the free nitrophenols, and probably nontoxic. Therefore, as long as they remain stable, these materials do not have the objectionable features of the nitrophenols. Yet, when a fungicide is needed for protection of leather, which is only when the leather is exposed to warm and humid conditions, free 4-nitrophenol is generated through the hydrolysis reaction. This reaction is accelerated by the same conditions that favor mildew attack, thus providing a mechanism for timely conversion of nontoxic to fungitoxic material.

All the compounds used in this investigation, and probably hydrolyzable 4-nitrophenyl complexes in general, are effective leather fungicides. Further exploration of these and other hydrolyzable 4-nitrophenol compounds to find compounds of optimum hydrolytic stability and permanence is one of the more promising approaches to the leather fungicide problem.

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Received May 7, 1960.

DISCUSSION

CHARLES W. MANN (Quartermaster R & E Command): I would like to congratulate Mr. Dahl on a fine job of presenting the results of recent work on the new technique which he developed and presented to us last year on the evaluation of fungicides for leather. His technique shows the advantage of using a scientific method to evaluate materials, to replace the old trial-and-error methods that have been so widely used in this particular field.

He has shown the importance of two characteristics—the rate of hydrolysis and the volatility—in evaluating the permanence of fungicides as well as their effectiveness. The results of this study extend the range of materials for use as fungicides, and I think they may enable us to obtain an ideal type of fungicide that lacks the disadvantages of color and so forth that we find in the common ones.

It is interesting to see that some of these materials are available in more or less inert form until they are needed, as indicated by the hydrolysis curves.

Again we see that chloronitrophenol rates fairly good as a fungicide. The ester converted over into this material also proves to be very effective. From the standpoint of low concentration some of these materials are much more effective than paranitrophenol. The one thing—important in any fungicide—that is not presented on these fungicides today is information on the toxic effects. Two of these materials are being investigated for toxic effects by the Quartermaster at the present time. When these results are available, it may be possible to allow their use as alternate fungicides and to extend the range of concentration, which will be a big advantage from a production standpoint.

J. N. ORIETAS (Albert Trostel & Sons Co.): During what stage, and how, did you incorporate these materials into the leather?

MR. DAHL: These were laboratory methods. We incorporated them in the leather from solution. We don't know how it should be done in a tannery. That has to be worked out. The nitrophenol is incorporated into the leather in greases, and I don't see why the same could not be done with these esters. However, a nonaqueous medium probably must be used.

RICHARD JENKINS (Dow Corning Silicones, Ltd.): I noticed from the results that you gave on the blackboard that nothing was said about the effect of the chlorine on the benzene ring there. I would assume that the chlorine is affecting the rate of hydrolysis and is contributing more to the fungicidal effect than perhaps the availability of nitrophenol.

MR. DAHL: You are right. The 2-chloro-4-nitrophenol is more potent than the 4-nitrophenol, and the same is true with the respective esters.

MR. JENKINS: Has anything been done with the fluorinated benzene ring?

MR. DAHL: Not as far as I know.

DR. PETER R. BUECHLER (Rohm & Haas): One thing occurs to me in trying to reconcile the rates of hydrolysis with the different amounts you find remaining at the end of your test period. Phenols, and possibly also these phenols, have been found to have a tanning action. It may be that the removal is not so much by volatilization as it is by the combining of the phenol with the hide substance. It could throw a monkey wrench into your studies.

MR. DAHL: I have quite a bit more data that I did not give here. We know that 4-nitrophenol is actually fixed in a leather. We have known that for a long time, and to analyze for it we have to add water to extract it with chloroform. If you do not add water, it is not extracted. We thought it was fixed through the hydroxyl group, possibly. But our paper, when it is published, will have data showing that these esters acted exactly the same way. They were also fixed in dry leather. You had to add water to the leather to extract them with chloroform. Now after extracting them once with chloroform, after the leather was wetted like that, we extracted them a second time—put in water again and extracted them. And there was never a case where any additional nitrophenol was extracted. So I think we got it all. If you used very dry leather—dried in an oven at 100° for 16 hours and then transferred to an extraction thimble—then something like 80% or 90% was left and did not extract.

The fixation that occurred in leather, I think, is a physical one. I think the fungicide, when you deposit it from solution as we did, is deposited on the surface of the fibers, and then you wet the leather or put it in a tropical room to absorb moisture and soften the fibers, and the fungicide enters into the fiber. Then on subsequent drying they are simply trapped in there. That is the kind of fixation that I think has happened, although it might be like a tanning action. The phenol probably tans, too. But it is a fixation, I think, that can be broken.

WILLIAM T. RODDY (University of Cincinnati): The paranitrophenol serves very well as a fungicide. On the other hand, it does not prevent hydrolytic deterioration of the leather fiber. The chloro-nitro phenols have the advantage of not coloring the leather or giving a yellow color on the alkaline side. Do they also prevent hydrolysis of the leather?

MR. DAHL: I don't have any data on that.

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25 YEARS AGO

The September, 1935, *Journal* contained the following papers, all presented at the Thirty-second Annual Meeting in Skytop, Pa., in June, 1935.

Analysis of Miscellaneous Tannery Materials Committee Report, by V. J. Mlejnek.

Tannages and Treatments Resistant to Acid Rot, by R. W. Frey, chemist, and C. W. Beebe, assistant chemist, Hide, Tanning Material, and Leather Investigations, Bureau of Chemistry and Soils, U. S. Department of Agriculture.

Studies in Chrome Liquors—Part IV. The Chemical Characteristics of Some Sucrose-reduced Liquors, by Edwin R. Theis and E. J. Serfass, Dept. of Chemical Engineering, Lehigh University, Bethlehem, Pa.

Each fall millions of Americans response generously to the call of their United Fund, Community Chest, Good Neighbor Fund, or similarly named United way campaign. Last year they gave a combined total of $455 million to support 28,000 voluntary health and welfare agencies serving 81.3 million men, women and children.

The day the fuel cell steps out of the laboratory commercially may be within five years, say the experts.

Current research, costing an estimated $30 to $40 million annually, foreshadows this electricity-producing system as the power plant of tomorrow. Special applications are seen in the immediate future but large central power generating plants are among the promising research possibilities. Some expectations have it that the cell will return the electric automobile to the nation's highways.

The fuel cell as a power plant is unique. It converts chemical energy directly into electricity with an efficiency rated at better than twice that of the most efficient power plants now available. The standard flashlight battery is a common example of the fuel cell principle. In such a battery, however, the chemical energy to be converted is stored in the cell. But the fuel cell is a converter, theoretically capable of producing electricity as long as fuel and air are supplied. In effect, it is a power plant system: the battery is a package of energy which eventually becomes exhausted.

Researchers have come up with a number of usable fuels for the cells. However, most reported fuel cell work to date has centered on hydrogen as the fuel and oxygen as the oxidant, or a mixture of hydrogen and a hydrocarbon as the fuel, plus oxygen.

—*Chemical News*, May-June, 1960.

THE EFFECT OF HIDE LOCATION AND CUTTING DIRECTION ON THE TENSILE PROPERTIES OF UPPER LEATHERS

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ABSTRACT

Previous authors published data showing the effect of hide location and cutting direction on some of the tensile properties of upper leather. The leathers used covered a wide range of hide sizes and tannages. When the tensile strength data were recalculated to a common base and plotted together, all the skins cut parallel to the backbone showed the same general pattern of variation over the hide, and the skins cut perpendicular showed a different but equally definite pattern of variation from one hide location to another. There was a definite indication that a natural pattern of variation exists which is the same for all bovine hides regardless of the age or size of the animal from which the skin was taken or the method used in tanning.

A program of tests was run to determine whether or not this indication was correct for the tensile strength as well as for the maximum elongation, resistance to stretch at low stress, and resistance to stretch at high stress. The test results show that the tensile strength and the resistance to stretch at high load follow the same pattern of variation that was indicated in the above tests, but the pattern of variation for the resistance at low load and for the maximum stretch vary according to a warped pattern which seems to result from the slicking operation at pasting. In addition, a method of sampling and of data analysis was used which seems to show the directions in which a specimen must be cut, at any given hide location, to obtain either the maximum or the minimum value of the tensile strength or other tensile property.

INTRODUCTION

Investigators have shown that almost every measurable property of leather varies from one skin location to another and with the direction in which the property is measured. The literature contains many papers that

deal with some aspect of the variability of leather. A complete review of literature on the subject is not necessary in a paper such as this. Reference will be made to three publications only; one by Wilson (1) over thirty years ago, and the others more recently by Mann (2) and by Kanagy (3). These articles all deal directly with the differences which occur in the tensile properties of leather due to location and orientation of the specimen in the hide.

Mann's published data are based on tests of 30 large chrome-tanned steer sides. Kanagy's work was done on 15 chrome-retanned cow sides and 15 chrome-retanned steer sides. Both investigators cut each side into 21 blocks, as illustrated in Fig. 1, and made tests on specimens cut from each block parallel to and perpendicular to the backbone. The elongation under a load of 100 pounds per inch of width and the tensile strength, were determined.

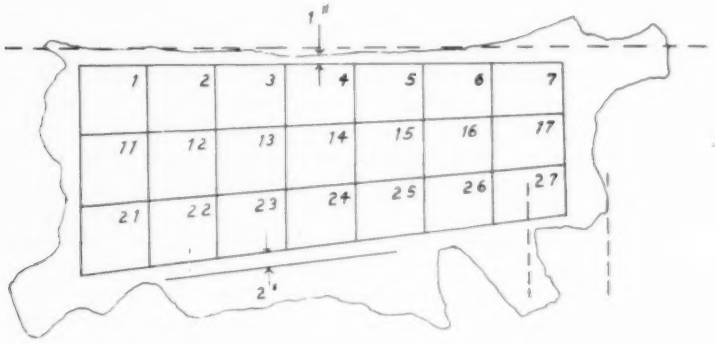

FIGURE 1.—Location of specimen blocks as used by Mann. Adapted from diagram in *JALCA*, **46**, 248 (1951).

Wilson used four small unsplit calfskins; two were chrome-tanned, and two were vegetable-tanned. One complete skin of each tannage was cut into tensile specimens with the long axis parallel to the backbone. The other two skins were cut with the long axis of the specimens perpendicular. He presented his data as diagrams of the skins showing the location and cutting direction of each specimen with the thickness, tensile strength, and elongation of each specimen noted on the drawings. In order to compare Wilson's data with those of Mann and Kanagy, his data diagrams were broken up into blocks of four specimens each, as shown in Fig. 2A for specimens cut parallel to the backbone and in Fig. 2B for specimens cut perpendicular. These blocks are located in the skin as closely as possible to the block positions used by Mann and Kanagy.

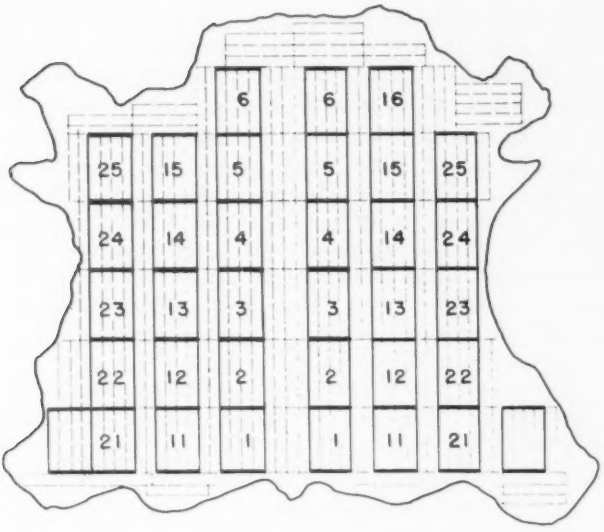

FIGURE 2A.—Parallel grouping of Wilson's data. Adapted from diagrams in J. A. Wilson's *Chemistry of Leather Manufacturing*, 2nd ed., Vol. II, pp. 1056–57.

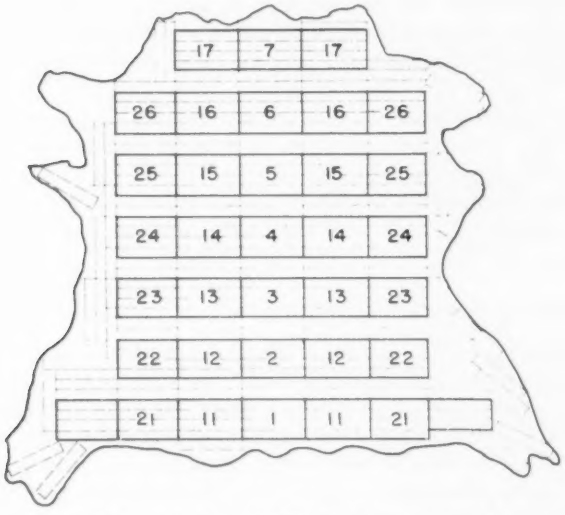

FIGURE 2B.—Perpendicular grouping of Wilson's data. Adapted from same source as Fig. 2A.

The tensile strengths of the four specimens in a block, such as Block #1, Fig. 2B, which crosses the backbone, or the eight specimens in a pair of blocks, such as the two blocks #13 located similarly on the two sides of the skin, were averaged to give the tensile strength at each skin location.

The data in these three papers were obtained from tests on five separate lots of skins which varied widely in size and tannage. Some of the leathers were considerably stronger than others, and when plots of the strength at various hide locations were made for the individual leathers, the curves were widely separated. This separation was eliminated when the block averages were divided by the average strength of the whole skin from which the block was cut, giving a series of ratios which varied in the same manner as the tensile strength varied from one skin location to another. These ratios for specimens cut parallel to the backbone are plotted in Fig. 3A. The ratios for each leather are plotted as dotted lines between a particular type of point so the curves for each leather can be followed. The heavy line on the chart is the average of the ratios for the five leathers. The skin diagrams at the bottom show the skin locations from which the plotted data were taken.

Fig. 3A shows that the tensile strength of all five leathers, when measured parallel to the backbone, varies from one skin location to another according to a fairly definite pattern. Fig. 3B shows a different but even more definite pattern for specimens cut perpendicular to the backbone. These two plots indicate that the tensile strength of leather made from all bovine hides will vary from one skin location to another according to a definite natural pattern, which appears to be the same for calfskins, cow sides, and steer sides, and for vegetable, chrome, and chrome-vegetable-retanned leathers.

It should be emphasized that the above conclusion is drawn for the tensile strength only. The tensile strength is an ultimate property, determined from the load which broke the specimen. At this load all residual leather stresses of lower order which might have been left in the leather after drying, staking, or other tannery processes have been overridden, and only the true fiber strength remains.

MAXIMUM AND MINIMUM VALUES OF THE PHYSICAL PROPERTIES

It is common practice in testing leather to cut specimens either parallel or perpendicular to the backbone. While this is a convenient way to establish a fixed orientation in the skin, there is no reason to assume that specimens so cut will give either the maximum or the minimum value of a given property at the cutting position. At each skin location there must be some direction along which specimens can be cut to give the average maximum value of a given property; and by the rules of symmetry it would be expected that specimens cut in a direction perpendicular to the maximum would give the

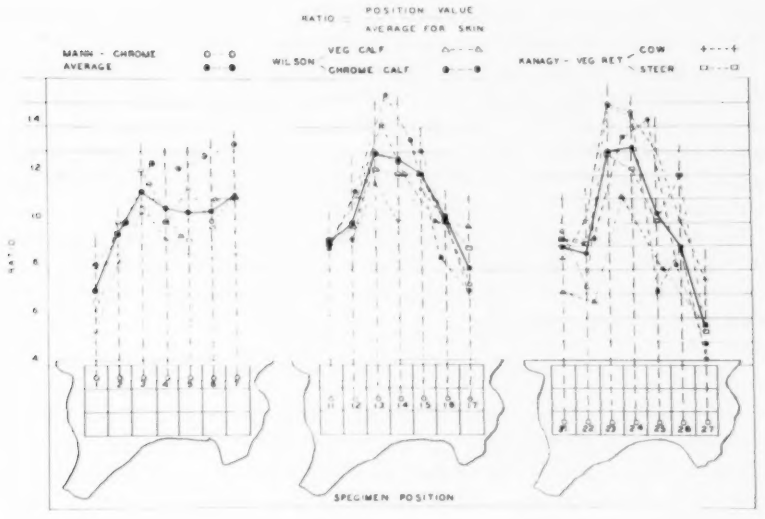

FIGURE 3A.—Tensile strength—parallel.

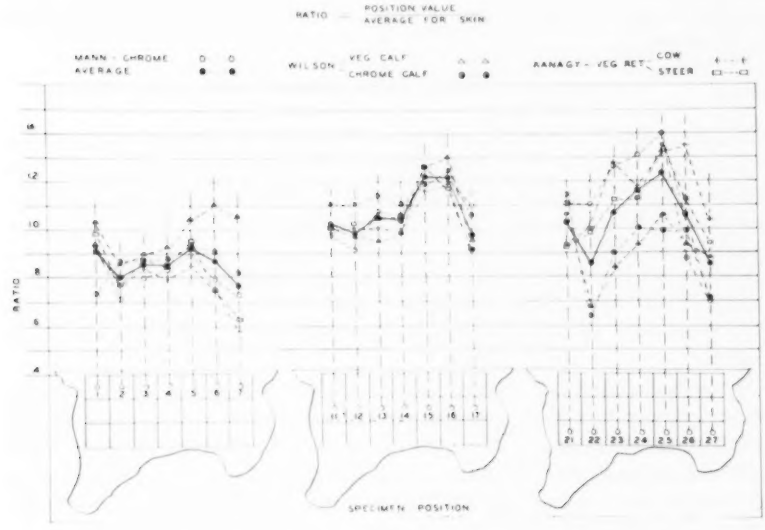

FIGURE 3B.—Tensile strength—perpendicular.

minimum value of the same property. These two values can be designated as the principal values of the property at each skin location.

The angle between a fixed base line, such as the backbone, and the direction along which specimens must be cut to obtain the maximum principal value of a property can be designated as the principal angle. There may be a different principal angle for each property at each skin position, i.e., the principal angle for the tensile strength will not, necessarily, be the same as the principal angle for some other property such as the elongation.

Neither Wilson, Mann, nor Kanagy made any attempt to find either principal values or the principal angles of the properties which they determined. In fact, their data, having only two components, could not have been used to make such a study.

PHYSICAL PROPERTY ELLIPSES

At any given hide location the average value of any property in each of three known directions relative to the backbone line can be found by test. These three components can be plotted as vectors from a common point and their ends will determine an ellipse in which the major axis is a vector for the maximum principal value and the minor axis is a vector for the minimum principal value of the property. (A mathematical solution for such ellipses is given in the Appendix of this paper.) Such an ellipse drawn for the tensile strength will thus determine the maximum strength of the leather at the location in question as well as the direction in which the specimens must be cut to obtain it.

TEST PROGRAM

A test program was planned to obtain the necessary data to use the elliptical method in determining the principal values of the tensile strength, resistance to or modulus of stretch at low and at high stress, and maximum stretch at failure at various skin locations for a common grade of chrome-tanned upper leather.

Twenty-one average quality chrome-tanned and pasted kips were purchased for the tests. The skins varied in area from 12½ to 14 square feet. They were split all over to between 37 and 45 mils and were completely finished.

The skins were laid out in 5¼″ square blocks as illustrated in Fig. 4. The spaces between the blocks were increased in large skins and decreased in small ones as necessary to keep the blocks in the same skin locations. No badly warped skins were used.

The skins were stored in an atmosphere held at 23°±1°C. and 50±2% relative humidity for several weeks before the tests were started. All the cutting, measuring, and testing were done in this same atmosphere.

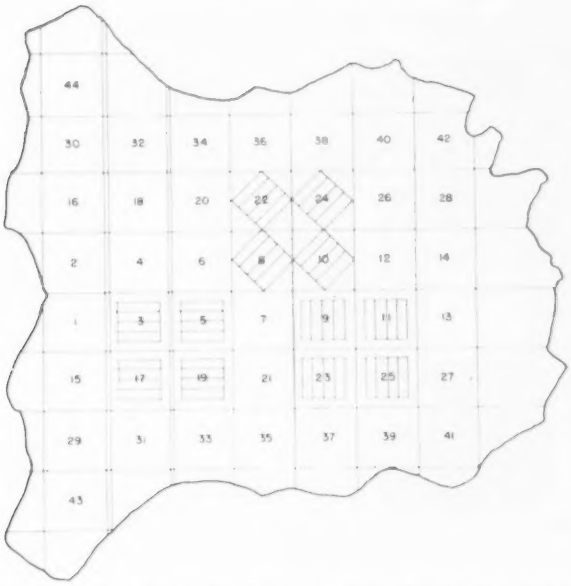

FIGURE 4.—Layout of skin showing three component directions in which specimens were cut.

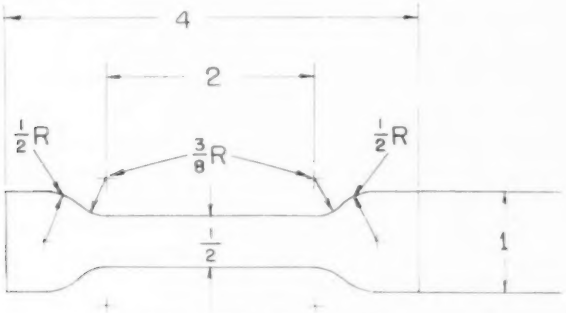

FIGURE 5.—Tensile specimen.

Four tensile specimens were cut from each block. Seven full skins were cut with the long axis of the specimens parallel to the backbone. In another seven skins the specimens were cut perpendicular to the backbone. In the seven remaining skins the specimens were cut at 45° to the backbone, with the two sides of the skins cut in a mirror view of each other so that the long axis of all the specimens ran from the backbone toward the belly and forward toward the shoulder.

FIGURE 6.—Instron Testing Machine.

This was a large test program. A total of 3696 specimens were cut, measured, and tested. Four physical properties were obtained for each specimen, making a total of 14,784 separate determinations which had to be averaged and evaluated.

The specimens were all cut with the same die, the dimensions of which are shown in Fig. 5. A clicking machine with a flat aluminum cutting pad was used, so the specimens were cut clean and accurately to the shape of the die. The width of all specimens was taken to be ½″ without being measured. The specimens were numbered as cut, and their thickness was measured at the center with a dead-weight gauge and recorded. All tests were made on an autographic Instron Testing Machine, Fig. 6, equipped with self-gripping jaws. The distance between the jaws at the start of the test was 3″. A crosshead speed and a chart speed of 4″/min were used.

Three typical load displacement curves were traced from the machine plots and are shown in Fig. 7. The top curve is for a specimen with a high modulus of stretch, the middle curve is for an average specimen, and the lower curve is for a specimen with a low modulus. The short horizontal lines on the curves are machine pips marking the curve at each 0.10″ increase in the distance between jaws.

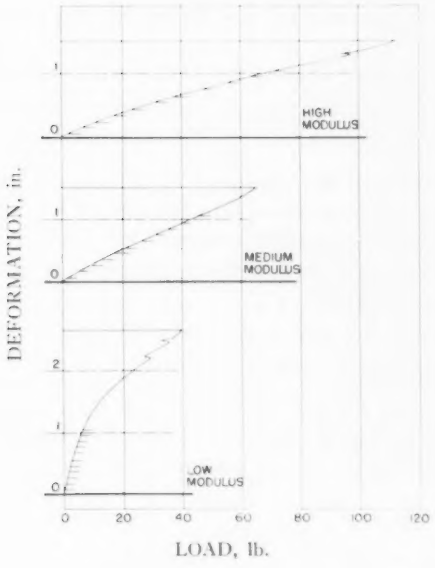

FIGURE 7.—Load-deformation diagrams.

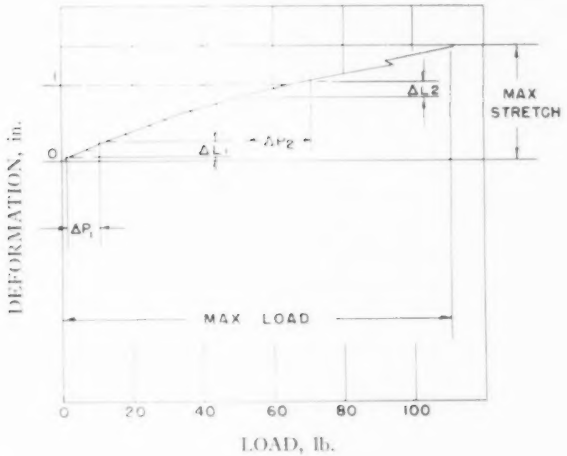

FIGURE 7A.—Instron readings.

The following values were read from the machine chart as shown in Fig. 7A.

1. The maximum load from which the tensile strength was calculated.
2. The maximum stretch at the instant of failure from which the percent elongation was calculated.
3. The load, $\triangle P_1$, and the elongation, $\triangle L_1$, from which the resistance to stretch or the modulus of stretch at low stress was calculated. An initial machine head motion of 0.10″ was used to make certain that the specimen was gripped properly and fully under stress before the measurement of $\triangle P_1$ and $\triangle L_1$ began.
4. The load, $\triangle P_2$, and the elongation, $\triangle L_2$, from which the modulus of stretch at high stress was determined.

The physical properties of the specimen were determined from the machine chart data as follows:

1. Tensile strength $= \dfrac{\text{maximum load}}{\text{original area}} = \dfrac{P}{A} = \dfrac{2P}{t}$

   where t = thickness of the specimen.

2. Percent elongation $= \dfrac{\text{maximum elongation}}{L} \times 100 = \dfrac{E}{3} \times 100$

   where 3 is the original distance between the jaws. This is not true value because the true effective length of the specimen is not known. But since all specimens have the same original shape and free length, this determination should give results which are fully comparable.

3. Modulus of stretch $= \dfrac{L\triangle P}{A\triangle L}$

   For the modulus at low load:

   L = distance between the jaws at the start of the reading = 3.10″

   $\triangle P_1$ = change in load necessary to increase the distance between jaws from 3.10″ to 3.30″.

   $\triangle L_1 = 0.20''$

   A = area of the specimen $= \dfrac{t}{2}$

   And for these tests $M_1 = \dfrac{31\triangle P_1}{t}$

For the modulus at high load:

$L = 3.80''$

$\triangle P_2$ = change in load required to increase the distance between the jaws from 3.80″ to 4.00″.

$\triangle L_2 = 0.20''$

A was taken as the original area of the specimen $\left(\frac{t}{2}\right)$ as the area at the start of the measurements could not be determined, and $M_2 = \frac{38\triangle P_2}{t}$

The modulus values, like the percent elongation, are comparative values in which the true effective length of the specimen is not known, and the increase in length and the reduction in area, both of which are large as compared to the dimensions of the specimens, are not used in in the calculations.

EXPERIMENTAL RESULTS

Before considering the elliptical interpretation of the results of these tests, a number of interesting items which the data indicate will be discussed.

Comparison of the properties at the same location on the two sides of a skin.—The average tensile strength of the four specimens at each location on the right side of a single skin was calculated. Corresponding averages were obtained for the left side. The numerical difference between these averages was determined for each location. These differences were added to give a single sum for each skin, a sum that showed which of the 21 skins had the greatest total difference between the two sides. The skin with the greatest difference happened to be one of the skins in which the specimens were cut parallel to the backbone.

The data for this skin are plotted as a scatter diagram on Fig. 8. The crosses are for the specimens cut on the right side of the skin; the circles, for the specimens cut from the left; the dotted line connects the average of the four crosses; the solid line, the average of the four circles. As can be seen, the data at each hide location are all mixed up, and nowhere is there a clear difference in the tensile strength on the two sides of the skin. The agreement in the tensile strength between two sides of a single skin is generally much better than that between two adjacent blocks cut from the same side of the skin.

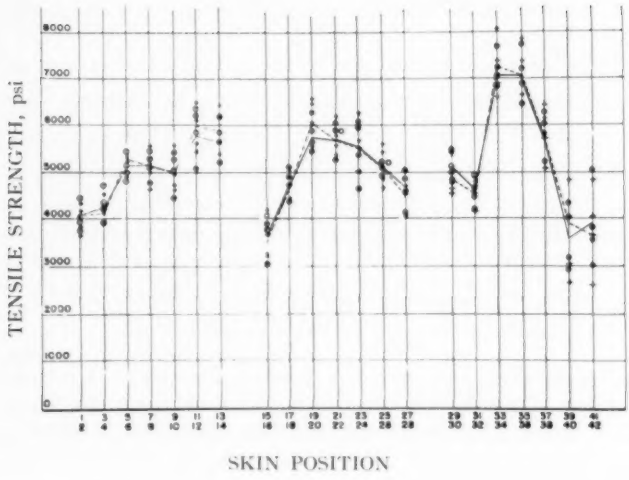

FIGURE 8.—Tensile strength. Parallel plot of eight values at each skin position for Skin 1.

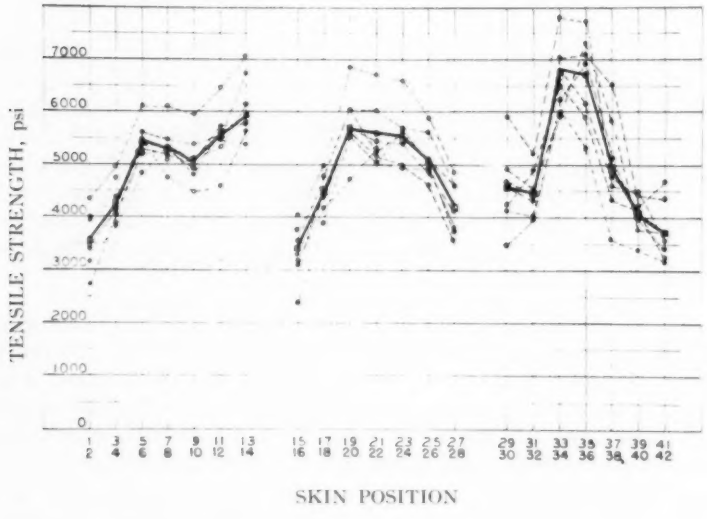

FIGURE 9.—Tensile strength—parallel. Seven individual skins 0- - -0; average 0——0.

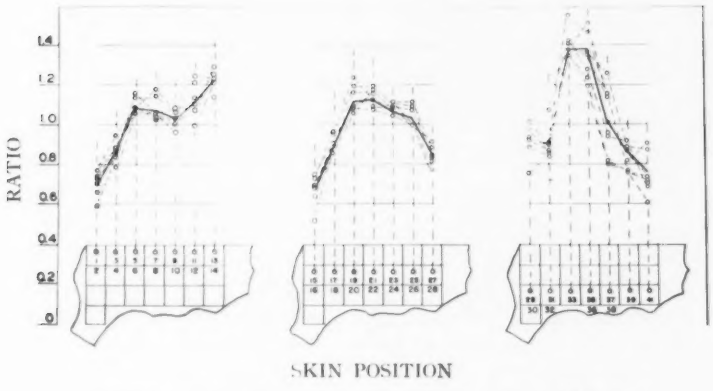

FIGURE 10.—Tensile strength—parallel. Ratio = $\frac{\text{position avg.}}{\text{skin avg.}}$

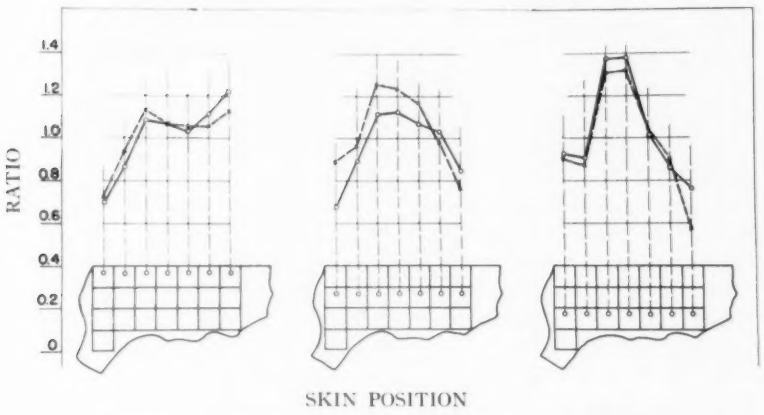

FIGURE 11.—Tensile strength—parallel. Ratio = $\frac{\text{position avg.}}{\text{skin avg.}}$
Wilson, Kanagy, Mann X- - - -X; test curve 0——0.

A similar analysis was made for the modulus of stretch at low load, the modulus at high load, and the elongation. It was found that the modulus at high load was very similar on the two sides of the skin, whereas the modulus at low load and the elongation were significantly different between the two sides at many skin locations. The nature and probable cause of these differences will be discussed when the ellipses of these last two properties are being considered.

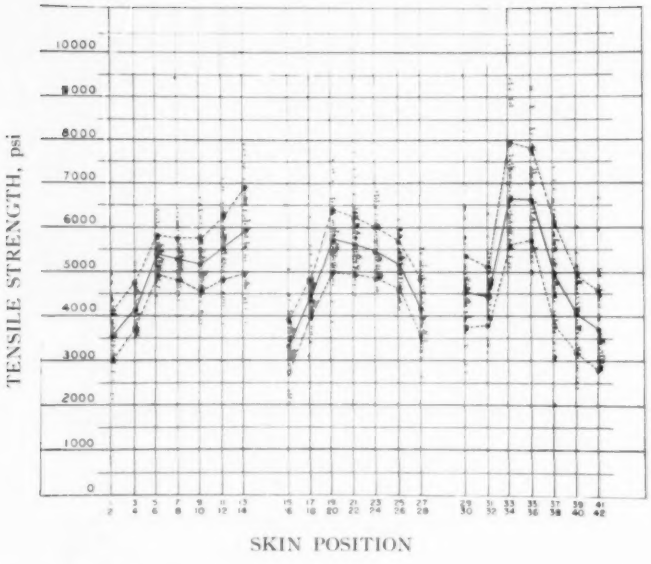

FIGURE 12.—Tensile strength—parallel. Central tendency 0——0; standard deviation envelope 0- - -0.

Comparison of the variation between the individual skins.—The average tensile strength of the 8 specimens cut from a pair of blocks in a similar position on two sides of a skin was determined for each of the 7 skins in which the specimens were cut parallel to the backbone.

These averages for each skin are plotted on Fig. 9. The circled points connected by dotted lines are the plots for the 7 individual skins. The average for the 7 skins is shown as a full line.

This plot shows that one skin is stronger than any other at nearly every hide location and that another skin is weaker at most positions; and yet the pattern of variation across the skin is very similar for each separate skin regardless of whether its over-all strength is high or low. Similar plots were made for specimens cut perpendicular and for those cut at 45° to the backbone. While the pattern of variation for each cutting direction was different, it was fully as definite as the pattern for the specimens cut parallel.

The ratio of the average strength of the 8 specimens cut at each hide location to average strength of the whole skin was found for each of the 7 skins. These values are plotted on Fig. 10. Because the spread between the individual skins is now eliminated, this plot shows even more clearly than Fig. 9 how closely the tensile strength of each skin follows a definite pattern.

The average curve of Fig. 3A and the average curve of Fig. 10 are plotted together on Fig. 11. The dotted lines between crosses show the average curve for the 5 leathers tested by Wilson, Mann, and Kanagy. The solid lines between circles show the curve of Fig. 10. The similarity between these curves is evident and indicates again that the tensile strength of leather varies over the skin according to a natural and well defined pattern.

Variability of the data.—An idea of the amount of variation which occurs in a lot of leather can be shown by plotting scatter diagrams of the data. Fig. 12 is such a diagram for the tensile strengths of the skins cut parallel to the backbone. At every position there is a wide variation between the strongest and weakest specimen. Skin location 5 and 6 has less spread in the data than any other; yet the tensile strength of the strongest specimen is 6400 psi, and that of the weakest is only 4400. At location 37 the tensile strength varies from 7400 psi to only 2000. The dark full line on the plot shows the way in which the central tendency of the data varies from one skin position to another. The standard deviation of the data for each hide location is plotted as crosses above and below the average. These points are connected by dotted lines to bring out their locations. The spread between these points shows the relative variability of the data at each skin position. The plot indicates a fact which is already well known: that there is less total variation in the bend than in other sections of the hide, and the greatest over-all variation exists in the flanks and belly.

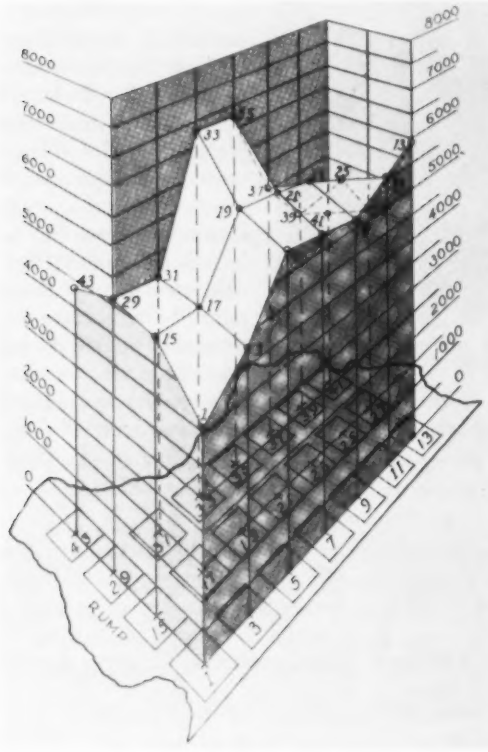

FIGURE 13.—Tensile strength (psi)—parallel.

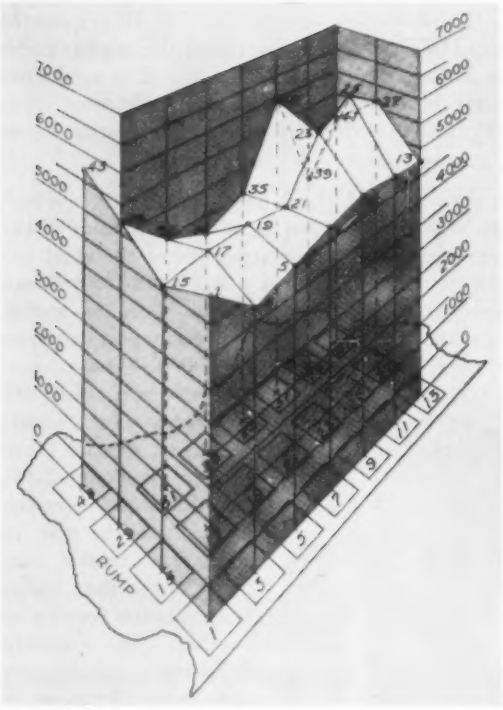

FIGURE 14.—Tensile strength (psi)—perpendicular.

Perspective plots.—A most complete picture of the way in which the strength of specimens cut in a given direction varies from one skin location to another can be obtained by making perspective plots of the test data.

Fig. 13 is a diagram representing the left side of a skin which has been laid out in blocks, then placed on a horizontal surface. From the center of each block a vertical rod is raised. The length of the rod is made proportional to the average tensile strength at that location. The top of each rod is connected to its adjacent rods by lines running in all four directions. The surface determined by these top lines gives an accurate photographic representation of the way in which the tensile strength of specimens cut parallel to the backbone varies in all directions over the skin.

Fig. 14 is a similar plot for specimens cut perpendicular to the backbone. It can be seen that there is less variation from one hide location to another in this plot than in the previous one.

Fig. 15 is a similar plot for specimens cut at 45° to the backbone. The variation between hide locations is much less for specimens cut in this direction than for specimens cut either parallel or perpendicular. It may be that a knowledge of this fact is of no value in the making or use of leather, but it should certainly be given consideration in cutting specimens for physical tests.

Study of the ellipses.

Tensile strength.—The ellipses for the tensile strength are shown on Fig. 16. There is a close agreement between the size and direction of the ellipses

at each location on the two sides of the skin. The ellipses on the right side of the skin are almost a mirror view of the ellipses on the left side.

If any axis of one of these ellipses is a true vector whose length is proportional to the average tensile strength of specimens cut in the direction of the axis, then several interesting facts regarding the variation in the strength of leather over a skin can be observed.

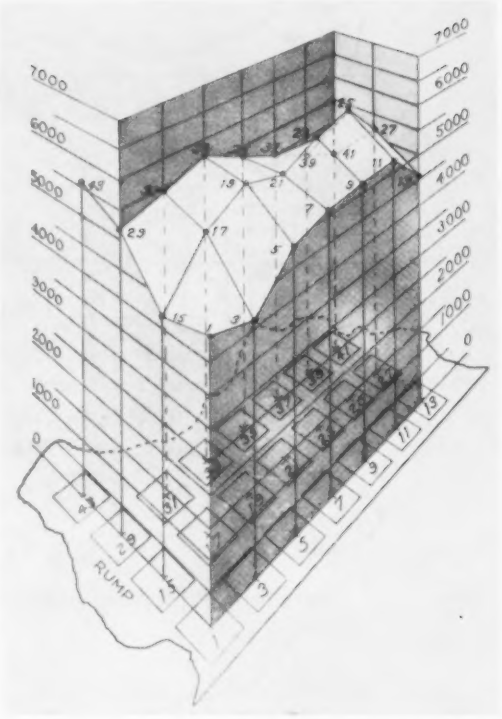

FIGURE 15.—Tensile strength (psi)—45° odd section.

1. The leather is strong where the ellipses are large and weak where the ellipses are small. The ellipses of Fig. 16 indicate that the leather is strongest in the belly and that the belly leather is comparatively strong in all directions. There is a band of strong leather running along the belly up and across the shoulders into the neck. The better leathers in the skin, that is, in the bend and in the rump, are comparatively weak.

2. Where the ellipses tend to be round, the tensile strength is only slightly affected by the cutting direction; but in those locations where the ellipses are more oval the direction of cutting will seriously affect the measured value of the tensile strength. There is one location, over the hip, where the ellipse is a true circle. At this location the direction of cutting will have no effect on the strength.

3. The cutting direction which must be used to obtain the maximum tensile strength at any hide location varies over the skin in a smooth flowing pattern except at one location just back of the front leg where a reversal of almost 90° from the adjacent blocks on all three sides is indicated; otherwise the

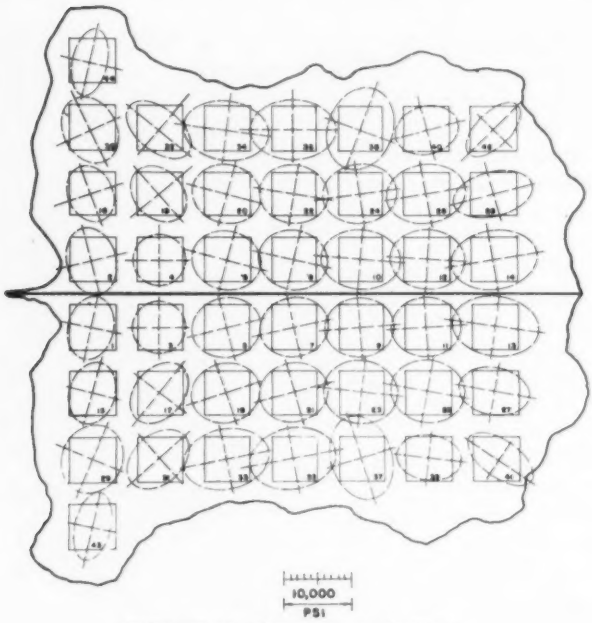

FIGURE 16.—Tensile strength ellipses.

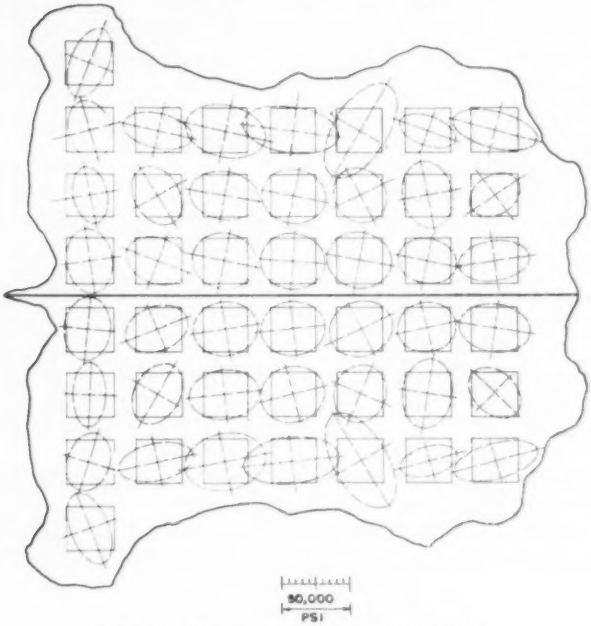

FIGURE 17.—Modulus ellipses at high load.

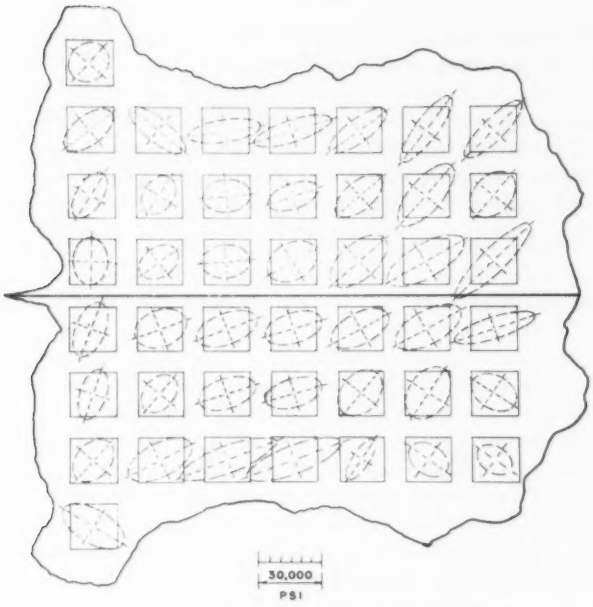

FIGURE 18.—Modulus ellipses at low load.

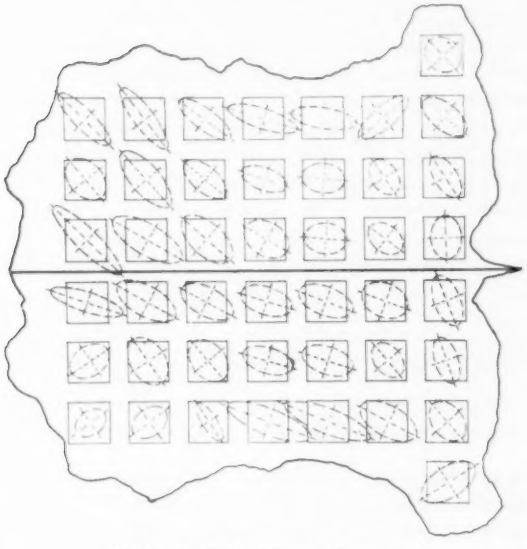

FIGURE 18A.—Figure 18 reversed.

pattern is smooth and could easily be followed in performing most tannery operations or in cutting parts from the skin.

Modulus of stretch at high load.—The ellipses for the modulus of stretch at high loads are plotted on Fig. 17. The values from which these ellipses were determined were measured between a stretch of 0.80″ and 1.00″. Under this condition of loading, the stress on a specimen was probably high enough to override any residual stresses that remained from the various tanning operations.

The pattern of these ellipses is very much like the pattern of the tensile strength ellipses. These ellipses are more oval than those for the tensile strength, but the angle between the major axis and the backbone is nearly the same for the modulus and tensile strength ellipses at most hide locations. The modulus ellipses, like those for the tensile strength on the right side of the skin, are almost a mirror view of those on the left side, indicating again that there is a natural similarity in the leather at the same locations on the two sides of a skin. The similarity between these ellipses and the tensile strength ellipses seems to indicate that the natural direction of greatest strength at a given hide location is also very close to the natural direction of the greatest resistance to stretch.

Modulus of stretch at low load.—The ellipses for the modulus of stretch at low load are plotted on Fig. 18. As can be seen, the shape and size of the ellipses and the direction of the major axis at many locations are not the same on the two sides of the skin. In this figure the grain side of the skin is seen with the flesh side away from view. If the figure is reversed and turned 90°, Fig. 18A, is obtained and the flesh side of the skin is in view as it would be on the pasting board. The plot shows a band of ellipses running from the lower left side of the skin across the backbone and toward the shoulder at the top right in which the long axes form a sort of flat *S*-shaped curve. A definite pattern has been established in the skin which is different from the smooth-flowing pattern formed by the major axes of the ellipses for the tensile strength and the modulus at high loads.

This warped pattern is probably the result of some strains or distortions the skin underwent somewhere in the tannery.

The peculiar *S*-shaped pattern of the low-stress ellipses most likely resulted from the way in which these particular skins were slicked down at pasting.

The pasting procedure was as follows: A skin was thrown on a horizontal board with the butt near one edge. Two pasters, one on each side of the board, reached to the center and placed their blades on the skin, then drew the blades toward themselves. As they came close to their bodies, the blades were

pushed slightly away and across their stomachs. This was repeated at least once and usually twice on each side of the first blade path. At this point the band of hide which was pasted down had almost the exact shape of the *S*-shaped curve shown in Fig. 18A. The rest of the skin was put down as each operator desired, but each man had developed a slicking pattern which he unconsciously followed quite faithfully, and the slicking patterns used could very well account for the orientation of the remaining ellipses.

The elongation ellipse.—The ellipses for the elongation are shown in Fig. 19. The major axes of these ellipses are almost exactly along the minor axes of the ellipses for the modulus at low stress. This indicates that the leather

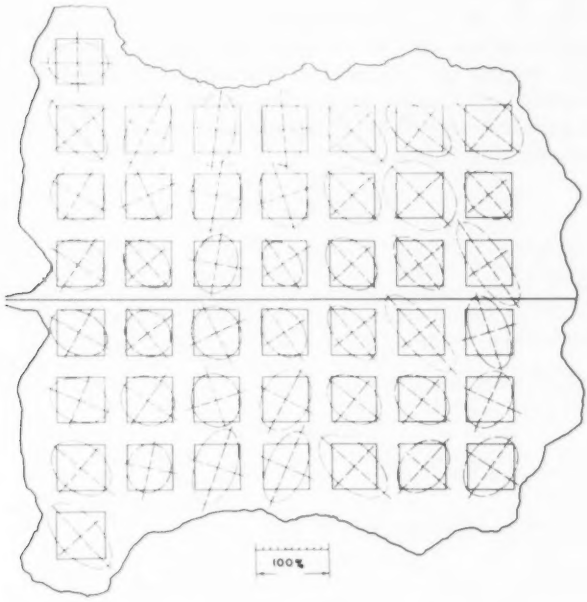

FIGURE 19.—Maximum stretch ellipses at different skin positions.

stretches the greatest total amount in the direction in which it has the least resistance to early stretch.

The pattern of these ellipses, like that for the ellipses for the modulus at low load, is probably determined to a large extent by the way in which the tannery performs the operation of pasting.

SUMMARY

Because this paper has dealt so exclusively with the tensile properties of leather, one might think that the author places great importance on these properties as a means of estimating the quality of leather at various skin locations or in a number of hides. This does not follow. He is well aware that the leather in the rump and bend—even though weak as compared to that in the belly—is considered of much higher quality and is much more desired for many uses. The tensile properties happen to be easily measured with good accuracy, and for that reason they are valuable in studying the pattern and the magnitude of the variations which occur in a lot of leather.

The test results coupled with the results published by Wilson, Mann, and Kanagy strongly indicate that the tensile properties of leather naturally vary over the skin according to a definite pattern which is the same for all bovine skins regardless of the age, sex, or size of the animal from which the skin is taken or the tanning procedures used in making the skin into leather. Any deviation which occurs in this pattern is probably the result of some tannery procedure which distorts the natural shape of the skin and leaves it with residual stresses and strains.

REFERENCES

1. Wilson, J. Arthur. *Chemistry of Leather Mfg.*, New York Chemical Catalogue Co., 1929; 2nd ed., Vol. 2, p. 1054.
2. Mann, C. W., *et al.* "Sampling of Side Upper Leather." *JALCA*, **46**, 228 (1951).
3. Kanagy, J. R., *et al.* "Variations of Physical Properties Within and Between Vegetable-retanned Cow and Steer Hides." *JALCA*, **47**, 726 (1952).

Received April 15, 1960.

APPENDIX

General Solution for an Ellipse in Terms of Three Known Components

In an ellipse

$B^2X^2 + A^2Y^2 = A^2B^2$ [General Equation]

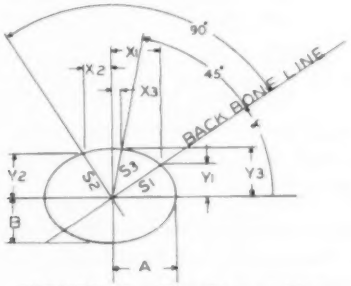

FIGURE 20.—The ellipse problem.

Then in Fig. 20

Let S_1 = length of any semiaxis of any ellipse
S_2 = length of the semiaxis at 90° to S_1
S_3 = length of semiaxis at 45° to S_1
α = angle between S_1 and the major axis of the ellipse
A = length of the major semiaxis of the ellipse
B = length of the minor semiaxis of the ellipse

For S_1:

$$X_1 = S_1 \cos \alpha$$
$$Y_1 = S_1 \sin \alpha$$

Substituting these values in the general equation

$$\cos^2 \alpha = \frac{A^2(S_1^2 - B^2)}{S_1^2(A^2 - B^2)} \qquad \text{[Eq. 1]}$$

For S_2:

$$X_2 = S_2 \cos (\alpha + 90) = S_2 \sin \alpha$$
$$Y_2 = S_2 \sin (\alpha + 90) = S_2 \cos \alpha$$

Substituting in the general equation

$$\cos^2 \alpha = \frac{B^2(A^2 - S_2^2)}{S_1^2(A^2 - B^2)} \qquad \text{[Eq. 2]}$$

For S_3:

$$X_3 = S_3 \cos (\alpha + 45) = \frac{S^3}{2} (\cos \alpha - \sin \alpha)$$

$$X_3^2 = \frac{S_3^2(1 - 2 \sin \alpha \cos \alpha)}{2}$$

$$Y_3 = S_3 \sin (\alpha + 45) = \frac{S^3}{2} (\sin \alpha + \cos \alpha)$$

$$Y_3^2 = \frac{S_3^2 (1 + 2 \sin \alpha \cos \alpha)}{2}$$

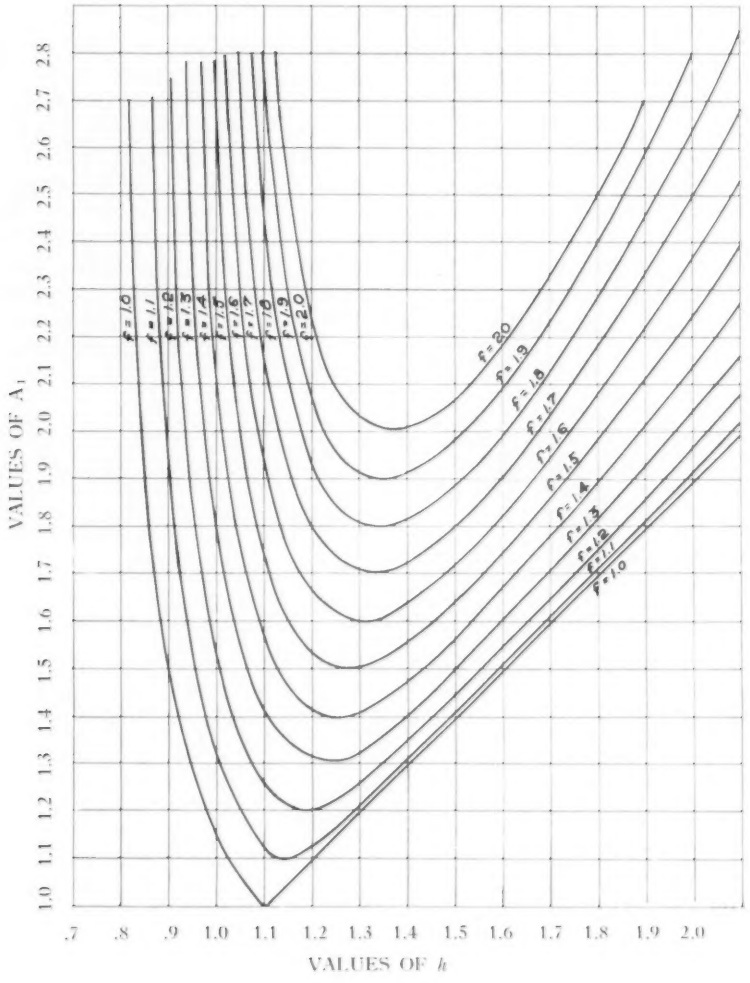

FIGURE 21A.—Values of A_1 where the major axis of ellipse $A = A_1 S_1$ and $f > 1$.

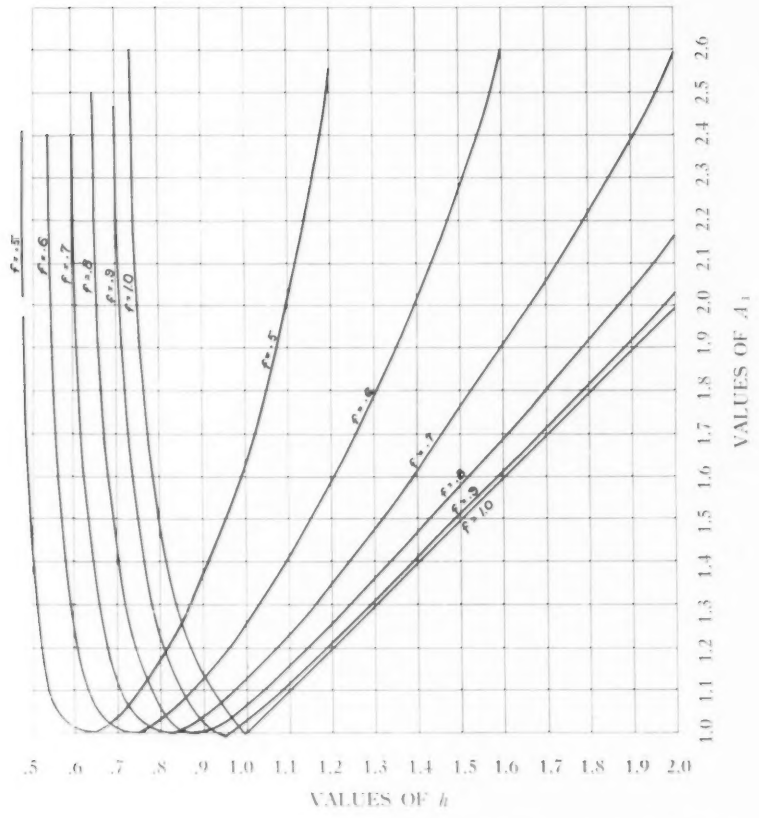

FIGURE 21B.—Values of A_1 where the major axis of ellipse $A = A_1 S_1$ and $f<1$.

Substituting in the general equation

$$2 \sin x \cos x = \frac{2 A^2 B^2 - S_3^2 (A^2 + B^2)}{S_3^2 (A^2 - B^2)} \qquad \text{[Eq. 3]}$$

Solving equations 1, 2, and 3 using the following equivalents:

$S_2 = fS_1$
$S_3 = hS_1$
$A_1 = A/S_1$
$B = B/S_1$

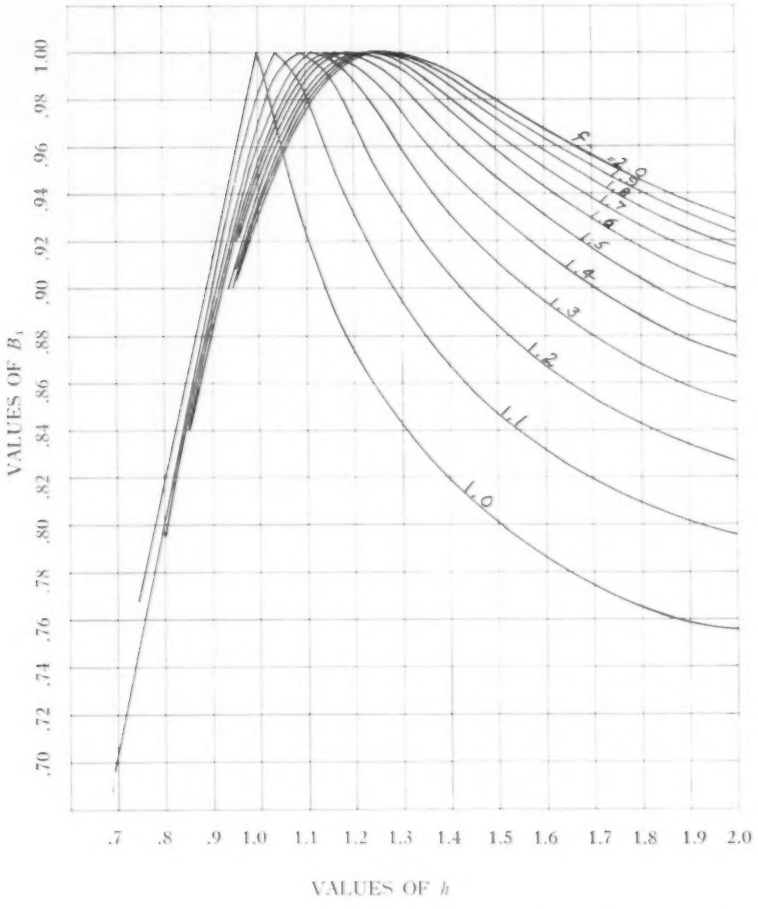

FIGURE 22A.—Values of B_1 where the minor axis of ellipse $B = B_1 S_1$ and $f > 1$.

$$B_1^2 = \frac{A_1^2 f^2}{A_1^2(1 + f^2) - f^2} \qquad \text{[Eq. 4]}$$

$$A_1^4\, 2\, f^2 h^2(2 - 2f^2 + h^2) - (4f^4 + f^4H^4 + h^4) - 4A_1^2\, f^2 h^2\, (1 + f^2) = 4\, f^4 h^4$$

[Eq. 5]

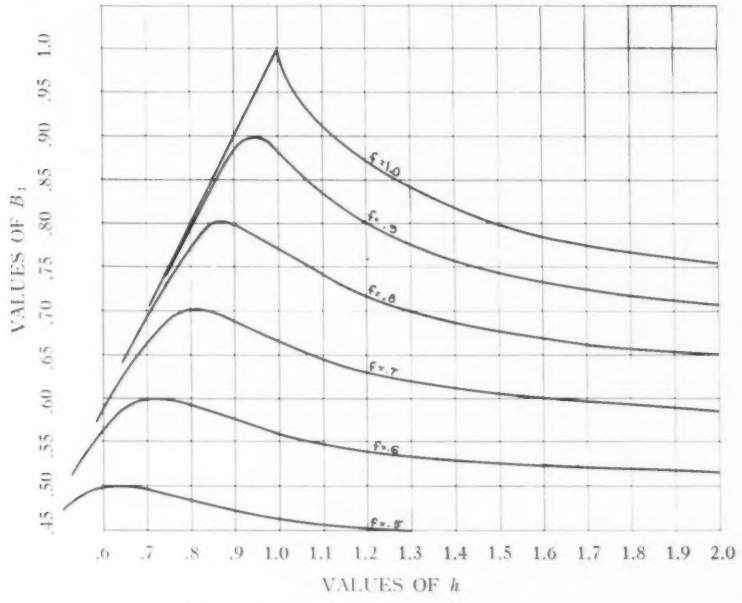

FIGURE 22B.—Values of B_1 where the minor axis of ellipse $B = B_1 S_1$ and $f<1$.

$$\text{Tan } \alpha = \frac{h^2 (1 + f^2) - 2f^2}{h^2(f^2 - 1)} \qquad \text{[Eq. 6]}$$

These equations were solved for various values of f and h, and the results plotted in Figs. 21 to 23 inclusive. The test results were entered on the plots and the values of A, B, and α were read directly.

The following problem is solved to illustrate the use of the equations and the plots.

Let

S_1 = 1950 psi = tensile strength at a given hide location parallel to the backbone.

S_2 = 2630 psi = tensile strength at the same hide location perpendicular to the backbone.

S_3 = 3220 psi = tensile strength at the same location at 45° to the backbone.

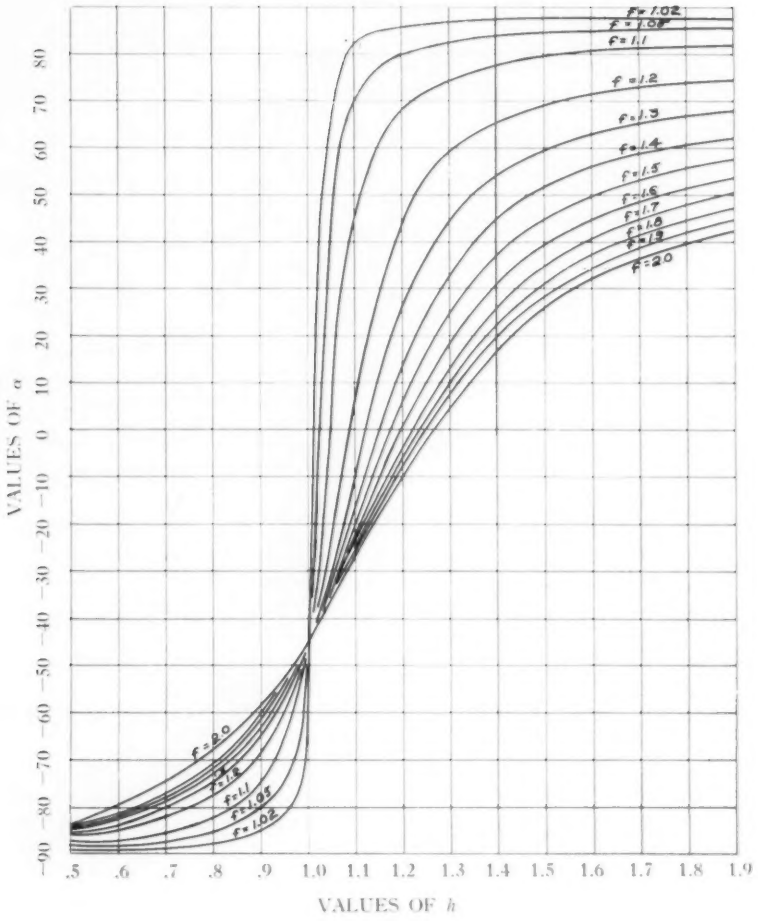

FIGURE 23A.—Values of angle α. $f>1$.

$$\text{Then } f = \frac{S_2}{S_1} = \frac{2630}{1950} = 1.35$$

$$h = \frac{S_3 = 3220}{S_1} = \frac{}{1950} = 1.65$$

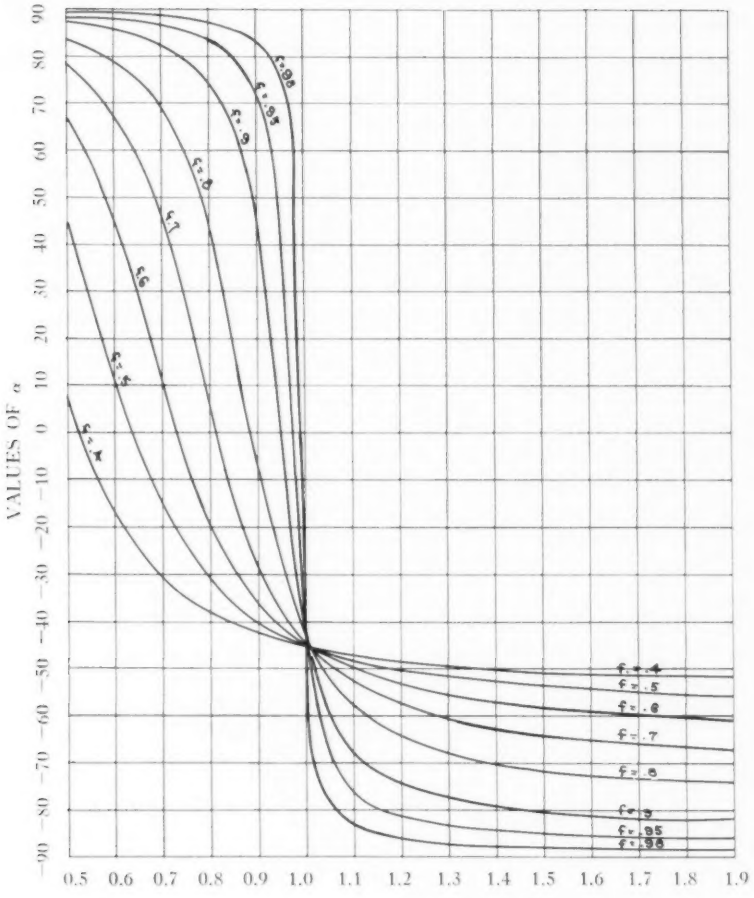

FIGURE 23B.—Values of angle $< f < 1$.

From Fig. 21a

$A_1 = 1.8$

From Fig. 22a

$B_1 = 0.897 = 0.90$

$B_1 = 0.897 = 0.90$

From Fig. 23a

$\alpha = 60°$

These values determine an ellipse in which the principal values are

$A = 1.80 \times 1950 = 3510$ psi
$B = 0.90 \times 1950 = 1760$ psi
$\alpha = 60°$ or $(90 + 60°)$

These principal tensile strength values and the component strength values are plotted on Fig. 24.

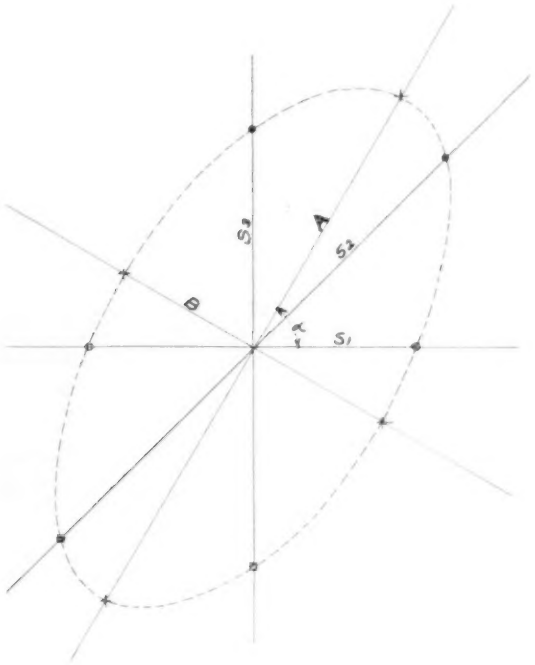

FIGURE 24.—The ellipse of tensile strength for the problem illustrated in the Appendix.

LIFE LINES

Brief Biographies of Our Contributors

SVERRE DAHL received his B. S. degree from Drury College, Springfield, Mo., and did graduate work at the University of Kansas City, Kansas City, Mo. Prior to joining the National Bureau of Standards in 1947, he worked for the Bureau of Reclamation at Fort Collins, Colorado, and in private industry in the midwestern states. Since coming to N.B.S. he has been active in the development of test methods for leather and has served on several ALCA committees. In addition, he has been engaged in studies on mildew-proofing treatments for leather. He joined ALCA in 1951.

DR. ARTHUR M. KAPLAN was graduated from the University of Massachusetts in 1939 and received his M.S. at the State College of Washington in 1941. Following World War II duty as a bacteriologist in the United States Naval Reserve (he attained the rank of Lieutenant Commander), he joined the staff of the Department of Food Technology at the Massachusetts Agricultural Experimental Station, Amherst. He earned his Ph.D. at the University of Massachusetts in 1948. From then until 1953 he served as microbiologist in Beltsville, Maryland, with the U. S. Department of Agriculture. Since 1953 he has been chief of the Microbiology Section, Chemicals and Plastics Division, Quartermaster Research and Engineering Center, Natick, Massachusetts. Dr. Kaplan's main interest at present is in the prevention of microbiological deterioration or contamination of materials.

MIETH MAESER—See the June, 1960, *Journal*.

"The rate at which science has been remaking the world is constantly accelerating. The past decade has seen more scientific advances than any lifetime before this decade, or than any century before the twentieth. This new science has not only had an impact on man's technology; it has influenced his total way of life, and particularly his mode of thinking. Education has been profoundly changed by these new intellectual horizons.

"This is particularly true of colleges dedicated to bringing the impacts of science to the daily lives of all people. Most of our curricula have changed in nature: descriptive or how-to-do-it courses have been replaced by those which emphasize basic scientific and mathematical concepts."

—Dr. John T. Caldwell, Chancellor of North Carolina State College.

ALCA NEWS

Proceedings, Reports, Notices, and News

of the

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CONGRESS OF INTERNATIONAL UNION OF LEATHER TRADES CHEMISTS

Plans for the biennial Congress of International Union of Leather Trades Chemists to be held in Washington, D. C., at the Shoreham Hotel, August 20–25, 1961, are already under way. Because of its international character and also because it is being held in conjunction with the ALCA meeting, the program is more extensive in scope and will last two days longer than our normal annual meeting.

The program will start on Sunday, August 20, with an informal presidential reception, which has become a fixture with our regular ALCA meetings. Dr. Harold G. Turley, former ALCA President and also former President of the International Union of Leather Trades Chemists, is chairman of the reception and will be in charge of the proceedings for that evening.

The technical program will include the annual John Arthur Wilson Memorial Lecture, specially prepared lectures by many invited guests, and possibly a seminar on the latest developments in applied technology on Friday, August 25. The chairman for the evaluation of manuscripts is Dr. Wallace Windus, assisted by Dr. Turley and Dr. Kanagy.

The chairman for the preparation of the technical program is Mieth Maeser, past President of ALCA.

There will also be a sprinkling of social events to enliven the proceedings; two afternoons have been set aside for this purpose. Several evenings will also be taken up with recreational events to further the creation of new friendships and better understanding among the various international groups attending.

Since an international meeting requires multilingual translation facilities, this item will certainly be an expensive feature of the whole program. There is a possibility, however, that a new Department of State building (to be opened next spring) equipped with the most modern facilities may be available to us if it is not required by the Department of State for that week.

The chairman has undertaken the task of raising the necessary funds to meet the expenses. He is most gratified to advise the membership that two Production Tanners' Clubs have already shown a willingness to help materially with funds. We are hopeful that another club will soon join them. In the meantime, several selected friends of our organization are being approached to make substantial contributions toward meeting the expenses. The ALCA is making available a substantial amount from its reserve fund for meeting the preparatory expenses, plus those required for a successful meeting.

The entire facilities of the Shoreham Hotel will be available to the members attending the Congress. It will be the first time that an International Meeting of Leather Trades Chemists has included all the attending members under one roof.

The rates at the Shoreham Hotel are:

$ 9.00 — single room
$14.00 — twin bedroom
$25.00 — suite
$ 4.00 — dormitory style (4 persons to a room)

Dr. Fred O'Flaherty, the Secretary-Treasurer of ALCA, is acting as Treasurer for this International Union Meeting. He will also act in his usual capacity in preparing the many details that are necessary for a successful meeting.

It is gratifying to note, also, the willingness of many members to act as volunteers in making the foreign visitors feel at home in their new surroundings. Since this will be the first time in its history that the ALCA will be host to the International Meeting, we are naturally hopeful that all members who can will be present and, if possible, contribute to the program. There is no question that with the usual dynamic spirit of our organization this meeting should be the most successful ever held under the auspices of the International Union.

DOMINIC MEO, JR.
Convention Chairman

COUNCIL MEETING MINUTES

Lake Placid Club
Essex County, New York
June 19, 1960

The meeting was called to order by President Maeser at 9:00 P.M. Members present were Messrs. Henrich, Retzsch, Somerville, Edmonds, Presley, Tetreault, Wederbrand, Windus, Meo, Turley, and O'Flaherty.

The minutes of the January 15 meeting were read by Dr. O'Flaherty. Council approved the minutes after adding that Council had requested that a check be made into the cancellation of the contract with Chalfonte-Haddon Hall in 1961.

The minutes of the February 12 meeting were read and approved with the following correction: That the Association has been retired from the obligation of holding their 1961 meeting at the Chalfonte-Haddon Hall without any penalty but are to consider this hotel when planning future meetings.

Mr. Wederbrand advised Council that the Association is operating within its income, but he is encouraging additional advertising. Mr. Wederbrand turned over three new advertising contracts to the Secretary.

Thought was given to the Association's future income. Mr. Wederbrand made a motion recommending that the incoming Council consider increasing the annual dues and subscription rates. This motion was seconded and approved by Council.

A motion made by Mr. Tetreault was seconded and approved, suggesting that the new Council give consideration to an increase of the secretarial budget.

Council considered listing the *Journal* advertisers with an acknowledgment of their support of the Association in the annual meeting program.

Mr. Maeser advised Council that Dr. Karl Gustavson has agreed to give the John Arthur Wilson Memorial Lecture in 1961.

Mr. Maeser advised that the Tanners Leather Show has moved its meeting date to June. He obtained its meeting dates for the next three years and although the dates fall very close to the ALCA meeting dates, they do not coincide. A suggestion was made that the Committee should keep the Leather Show in mind when planning future dates.

Mr. Maeser drew to Council's attention the large number of members dropped for nonpayment of dues and recommended that this trend be carefully watched. It was suggested that the new Council consider appointing a committee to study this trend.

Mr. Meo reported the progress being made on the International Meeting and informed Council of his committee chairmen. Mr. Meo agreed to prepare a written report which will be published in the *Journal* to keep all members informed.

There being no further business, the meeting was adjourned at 10:25 P.M.

Respectfully submitted,

FRED O'FLAHERTY
Secretary

June 22, 1960

The meeting was called to order by President Henrich at 1:50 P.M. The following members and guests were present: Messrs. Edmonds, Presley, Tetreault, Stubbings, Lollar, Wederbrand, Windus, Meo, and Roddy. Harold Y. Miller and Dr. Fred O'Flaherty were absent.

Dr. Henrich welcomed the new members to Council.

The minutes of the June 19 meeting were read and approved by Council.

Council accepted the Secretary's resignation and Dr. Henrich with Council's approval reappointed Dr. O'Flaherty as Secretary-Treasurer for another two-year term.

The Ways and Means Chairman's resignation was accepted, and Dr. Henrich with Council's approval reappointed Mr. Wederbrand to be the Ways and Means Chairman for another two years.

Dr. Henrich read the report of the Board of Tellers advising Council of the election results. The total number of ballots cast was 283 from a possible 552 active members eligible to vote. After discussing the low return of votes, Council recommended to the Secretary that the ballot be sent to the members at the latest date permitted by the By-Laws, and also that the Secretary should include the number of votes in his annual meeting report.

Dr. Henrich reported that most of the Technical Committees met during the annual meeting and the chairmen will send their reports to Dr. Stubbings, the new Technical Committee Coordinator.

A letter from E. L. Rayfield, Chairman of the Tannin Analysis Committee, was read advising Council that this committee has not been very active recently and suggesting it be discontinued. Mr. Rayfield also resigned as chairman. Upon a motion by Mr. Tetreault, Council voted to dissolve the Tannin Analysis Committee. Mr. Presley moved that the subcommittees of Determination of Lignosulfonates with S. Dahl, Chairman, and the Nontannins in Lignosulfonates with F. Marshall, Chairman, operate under the Vegetable Leathers Committee. This motion was accepted. Dr. Lollar has agreed to reorganize the Vegetable Leathers Committee. Resignations of Messrs. Henry Merrill and Ira Clarke from the Vegetable Leathers Committee were accepted.

Dr. Windus stated that the supply of papers on hand is satisfactory. Dr. Windus advised Council that he has released the summary papers of the Symposium to the trade papers.

Council agreed to include the summary papers of the Symposium panel as an introduction when publishing the Symposium. Ways to speed up publishing the Symposium were discussed, and Council advised the Secretary to request Mrs. Griffin to make by multilith or mimeograph enough copies of the Symposium so that one copy could be sent to each participant and ten additional copies to the Symposium Chairman.

Dr. Stubbings, reporting for the Convention Committee, advised that from the estimated expenses he now has he expects a loss of $150.00 for this Convention. The deficit occurred because there were not enough subscribers for the exhibit booths.

Council discussed the problem of some people attending the meeting but not registering. Dr. Stubbings has agreed to compare the hotel's registration list and the Association's registration list, then report his findings to Council at the next meeting.

Council discussed holding the 1964 meeting at the Chateau Frontenac in Quebec City or returning to the Lake Placid Club. Upon motion by Mr. Tetreault, Council voted to return to the Lake Placid Club on June 14–17. These dates were confirmed with the hotel by Dr. Stubbings with the second preference dates of June 21–24. Mr. Tetreault moved that the Association take the later dates if the first dates conflicted with the Tanners Council Meeting. Mr. Wederbrand will talk to Mr. Glass about the 1964 meeting dates.

Council asked Mr. Edmonds to advise the Chateau Frontenac of their decision for 1964 and that they will consider the site for a later date.

Dr. Henrich appointed the following Awards Committee:

Harold G. Turley, *Chairman*
Joseph R. Kanagy
Charles M. Morrison, Jr.

The committee is to consider candidates for the Alsop Award and the Winheim Award.

Dr. Henrich appointed the following Nominating Committee:

Frank Zeissig, *Chairman*
Herbert L. Ellison
Ernest H. Stein

Dr. John Highberger has agreed to serve as chairman of the committee appointed to select the 1962 John Arthur Wilson Memorial Lecturer. He will be assisted by Herbert Tetreault from the ALCA Council and another member appointed by Salem Oil and Grease Company.

Mr. Meo discussed the cost of the International Meeting in 1961. Mr. Wederbrand made a motion to poll by letter ballot the membership for their opinion of using $5,000.00 from the Association's General Surplus for the International Meeting if it is so needed. The motion was seconded by Mr. Presley and accepted by Council.

Council agreed to omit the award for an outstanding paper in 1961. The reserve established for sending the delegates to the International Meeting will be used in financing the meeting.

Mr. Meo read a tentative program to Council. The papers are to be of outstanding merit since it will include the annual John Arthur Wilson Memorial Lecture; lectures by invited guests of outstanding reputations; and, possibly, a Seminar on Friday, dealing with applied technology sometimes referred to as automation. Mr. Meo will meet with the hotel personnel in August and will advise Council at their next meeting about the exhibit space and power lines available to determine whether "automation" can be the theme of the exhibits.

Upon settlement of the 1960 convention funds, Mr. Wederbrand will transfer the Convention Fund to Dr. O'Flaherty, Secretary-Treasurer.

Mr. Carl Telander's resignation from the International Leather Analysis Commission was accepted.

Council discussed the practicability of the ALCA delegates remaining on the International Commission. The matter will be discussed further at the International Meeting in 1961.

Dr. Henrich read the following active membership applications which were accepted by Council: Messrs. Herbert Eastwood, Holm Rueffer, Howard Waller, Charles Coey, Herman J. Steinberg, Purdy Bradford, John R. Turner, Theodore W. Reed, Joseph Crowley, Raymond L. Hebert, Arthur J. McHiff, Mark N. Curgan, and Daniel P. Hourihan.

The following petition for transferring to active membership from associate was accepted: Walter May.

The next meeting of Council will be held on Wednesday, October 19, at the Edgewater Beach Hotel in Chicago, Illinois.

There being no further business, the meeting adjourned at 4:15 P.M.

Respectfully submitted,

FRED O'FLAHERTY
Secretary

Unless science and technology are pursued in the interest of human betterment, they remain an indulgence which no nation can afford.
—Albert Einstein

Obituaries

VIRGINIA RAU POWER

Virginia Rau Power died suddenly on July 6, 1960, of a heart attack. She was a chemist for Leas & McVitty, Inc. at the time of her death.

A graduate of Marshall College of Huntington, W. Va., she was a chemist for the Mead Corporation in Lynchburg, Va., from 1937 to 1955 as assistant to Charles R. Oberfell, E. S. Flinn, and Gene W. Stanbery. Upon the closing of Mead's Tanning Extract Division, she moved to Roanoke, Va., and was associated with Lester M. Whitmore and George V. Downing in the laboratory of Leas & McVitty, Inc.

She was active on the ALCA Committee on Copper Determination and Lignosulfonate Determination.

A member of St. Paul's Episcopal Church in Salem, she was active in the choir and other work. She was 43 years of age, and a member of ALCA since 1948.

LESTER F. PEABODY

Lester F. Peabody died at the age of 78 on Saturday, July 16, 1960, at a nursing home in New Jersey after an eleven-year illness. He had been an associate member of ALCA since 1923.

He had been an assistant superintendent at National Calfskin Company and superintendent at the Peabody branch of Griess-Pfleger Company. He was associated with the Ohio Leather Company from 1927 until his retirement in 1949 and became widely known throughout the shoe and leather trade. He was a vigorous and devoted worker for the Unitarian Church of Youngstown, Ohio, where his funeral was held on July 20, 1960.

He is survived by his wife, the former Lena Smith of Beverly, Massachusetts, and by two sons, Roger of Claymont, Delaware, and Donald of Verona, New Jersey, and by five grandchildren and two great-grandchildren.

ABSTRACTS

Judging Semichrome Leather on the Basis of Chemical Analysis. V. Kubelka and A. Blazaj. *Leder Kurier*, **3**, 246–52 (1959).—The degree of tannage of pure chrome-tanned leather can be calculated as for vegetable leather. For semichrome leather the degree of tannage is not sufficient for its characterization because its properties are influenced by the ratio of chrome to vegetable tannin. The total degree of tannage of semichrome leather is the sum of the degree of chrome tannage and the degree of vegetable tannage. It is difficult to determine both chrome tannin and vegetable tannin in semichrome leather. It would be advantageous if chrome tannin could be calculated from Cr_2O_3 content, and a factor, F, of 2.76 has been proposed for this purpose (*JALCA*, **54**, 48 [1959]). Before this factor can be adopted it will be necessary to establish its constancy. The size and composition of the chromium tanning complex in the leather depends on various factors such as temperature and basicity of the tan liquor, neutralization, effect of dyes and fatliquors, speed and temperature of drying, etc. The Cr_2O_3 content of semichrome leather, if expressed as percentage of leather, varies with the vegetable tannin content; it is only characteristic of the leather if calculated on the hide powder basis. To show the effect of the quality of chrome liquor on the factor, F, tannages were made with cowhide, and the leathers were analyzed in the rough, unfinished condition. For leather tanned with a chrome alum liquor neutralized with soda at boiling temperature, the value of F decreased from 3.71 to 2.88 as the basicity was increased from 0 to 25.3. When neutralization was at room temperature instead of at boiling, F decreased from 2.72 to 2.16 for practically the same basicity change. With a sugar-reduced bichromate liquor F decreased from 2.35 to 2.03 as basicity increased from 13.6 to 44.4. Variation of F is too great to permit its use for leathers prepared in different ways. Some data on effect of finishing were obtained as follows: Samples of semichrome sole leather were taken daily for 15 days from a tannery and analyzed in the uncolored, unfinished condition. The average F value was 3.29 (range 3.05–3.60). After dry storage for 12 months at room temperature the samples were reanalyzed. The F value was 3.54 (range 3.3–3.78). The samples were then soaked for 17 hours in water, dried to constant weight (5 hours) at 105°, and analyzed. The F value was 3.52 (range 3.22–3.92). I.D.C.

Fluorescence Colorations on Animal Skin Material. P. Stadler and W. Träsch. *Das Leder*, **10**, 213–6 (1959).—Fluorescence dyes are finding increased use in histological technics. A study of the effects obtained with such dyes was made with Zeiss equipment. A UG 5, 3-mm. filter was used to block out the 4000–6700 angstrom light, and a blue BG 12 filter to remove the remaining red light. After passing the specimen the remaining UV light was blocked by a GG 4 filter. The images had strong contrast because of the self-illumination of each part of the section. Holes in the specimen give off no light, so that the images resemble those found in dark field work. Paraffin-embedded or frozen sections may be used, and they may be fixed or unfixed. To color the sections they should be left for one hour in a dilute (usually 1:10,000) solution of the dye, rinsed, then left to dry slowly in the air. A nonfluorescent immersion oil should be used. The colors are quite stable. Nine figures are given to show colors that can be obtained on collagen, hair roots, etc., and a table lists the colors given by 24 dyes on collagen, elastin, keratin, muscle, and cell nucleus

materials. Staining is influenced by pH of the dye solution. At pH 1 auramine O stains epithelial parts and keratin bright green, but collagen is only faintly colored. At pH 8, however, collagen is green and the other two constituents have become yellowish. The same dye may give quite different colors on different skin constituents. Interpretation of the colors is difficult because the behavior of various fluorescence dyes with different parts of the skin has not yet been thoroughly investigated. Absorption of these dyes is prevented by vegetable tannin but not by chrome tannin. Penetration of vegetable tannin into hide can be followed by use of fluorescence dyes. I.D.C.

Conducting and Evaluating Sweat-Resistance Tests on Vegetable Insole Leather. G. Gran and F. Kolos. *Das Leder*, **10**, 207–13 (1959).—A study was made of the effect of time and temperature and of the changes in physical properties of leather during treatment with a lactate-urea solution. The artificial sweat solution contained 20 g. of salt, 20 g. of urea, 10 g. of ammonium lactate, and 1 g. disodiumphosphate per liter and was adjusted to pH 7.4–7.6. For a test, leather strips (5 x 10 cm.) were treated for 30 min. with 50 ml. of sweat solution at 40° in one series, and at 20° in a second series; then they were dried for 23.5 hours. These treatments were repeated on days 2, 4, 7, 10, 15, and 25. Comparable strips were treated in the same manner but with distilled water instead of sweat solution. Changes in color and stiffness were evaluated subjectively, and measurements were made of changes in area and in permeability to air and to water vapor. None of these methods were of value for measuring sweat resistance; the color changes were temperature effects, shrinkage in area was slightly decreased by the sweat solution, and permeability results were too scattered for conclusions. Water absorption, however, was influenced by treatment. As the number of treatments with water increased, absorption of either warm or cold water increased to a constant high value, but as the number of sweat treatments increased, absorption first increased (2 to 4 treatments) then fell to values below that for the orginal untreated leather. Absorption values corrected for absorbed sweat components showed the same effect as uncorrected values. The amount of sweat taken up per treatment was found from the weight of the treated, conditioned leather strips. The amount of sweat components leached out during a water absorption measurement was determined by titrating for chloride in the solution remaining after the test. A rapid method for determining resistance to sweat is the following: Cut side by side two 50 x 100 mm. strips of insole leather. Soak one strip for 30 min. in 50 ml. of sweat solution (as above) at 40°C., then dry for 23.5 hours at 55°C.; repeat 3 times; condition at 20°C. and 65% relative humidity for at least 3 days. Determine water absorption by the usual method after 15 min., and 1, 3, and 24 hours, and add these values to obtain A. Soak strip 2 in 50 ml. of water at 20°C. for 24 hours, dry at 20°, condition and measure water absorption as above to find B. Sweat resistance = R = 100 A/B. Resistance is considered good if R is over 85%, fair if it is between 70% and 85%, and poor if R is below 70%. I.D.C.

Tannage with Epoxy Resins. L. Villa. *Bull. Assoc. Franc. Chim. Ind. Cuir*, **21**, 123–24 (1959).—For several years numerous suggestions have been made to utilize macromolecular products for the impregnation of leather and as tannage and retannage agents. Often experiments were made with resins that were in a state of advanced polymerization, and the results were medi-

ocre and did not find industrial application. Polymerization *in situ* is feasible by fixing beforehand on the collagen fiber one of the polycondensable molecules of the future macromolecule. The polymer must have an affinity for the skin, either natural or as a result of treatment of the collagen before tanning, and besides must possess the possibility of polyaddition with other substances. For a first study, the epoxy compositions were chosen. These compositions are polymerizable and polycondensable, and the reaction temperature is low, often even ambient. A large number of epoxy resins are prepared starting with epichlorohydrin. The chloroepoxy is not only very reactive but also bifunctional. After recognizing the tanning properties of epichlorohydrin and the possibility of associating it with other tanning materials such as vegetable, quinone, chrome, iron, and aluminum, the polycondensation of the epoxy with 4-4′dihydroxydiphenyl 2-2′ propane was tried. This polymerization *in situ* was done as follows: After the classic beamhouse procedure the skin, delimed to pH 6, was submitted for 3 days to the action of a 10.0% solution of epichlorohydrin in aqueous alcohol. During tanning, starting from the second day, the pH is brought up progressively to 10. The tannage with epichlorohydrin is then terminated, the bath is drained, and the skin is rinsed with water and then dried. The skin is then treated for 2 days with a 10.0% solution of dihydroxydiphenyl propane in aqueous alcohol. The leather is not of great industrial interest but shows promise of development. The epoxy resin may be modified with organic acids, amines, amides, or polyamides, and with aldehydes. A mixture of epoxy resins with other polymers such as phenol, urea, and melamine formaldehyde, polyesters, acrylates, and vinyls is contemplated. R.H.

Note on the Finishing of Leathers for White Equipment. I. Julien. *Bull. Assoc. Franc. Chim. Ind. Cuir*, **21**, 114–16 (1959).—It has been observed that numerous leathers destined for the manufacture of white belts became yellowed when exposed to ultraviolet rays. In order to determine the different causes of the yellowing of leather a series of experiments were undertaken. The program consisted of a study of the behavior of the finishing only—this to be applied on plate glass or on chrome leather lightly fatliquored; a study of the influence of fatty materials in the leather; and a study of the influence of tannage. Before undertaking this, experiments were done on the method of application of finishing agents, their exposure to ultraviolet rays, and the evaluation of the changes. The experiments were done on two acrylic emulsions, two commercial cellulosic pigments, a plasticized cellulosic lacquer, and two titanium oxides. The products were tested separately and in combination on plate glass and on chrome leather and submitted to irradiation from ultraviolet rays for 15 hours. These conclusions were obtained following the first observations: the pigments alone and the lacquer alone did not undergo any notable change either on glass or on leather. In all other cases the tests showed changes, i.e., the white presented a yellowish tint more or less accentuated. R.H.

The Microflora of Tanning Liquors and of Vegetable-tanned Leather. J. Prevot. *Bull. Assoc. Franc. Chim. Ind. Cuir*, **21**, 116–22 (1959).—The flora in plumping liquors is numerous and consists of yeasts, molds, and bacteria. The study of yeast was done on 100 strains representing 19 species isolated from a diversity of sources and substrates. This study shows that 5 of the species are harmful to the infested plumping liquors. These are as follows: *Petasospora rhodanensis, P. strasburgensis, Pichia pseudopolymorpho, Candida*

guillermondii, and *C. humicola*. It was noted that all the strains representing these species do not offer the same aggressiveness with respect to the tannins. Thus, whereas the sources of *Petasospora rhodanensis* isolated by Boidin and Aladie were without action, those of Adzet destroyed the tannins. The harmful sources act in two ways: by hydrolyzing the tannins or by the formation of sediments which bring down the tannins. The study of molds shows that the most aggressive plumping liquors in our climate are as follows: *Aspergillus niger*, *A. flavus*, *Penicillium groupe frequetans*, and *Paecylomyces variati*. They hydrolyze tannins easily. With regard to vegetable-tanned leather, the yeast is without much interest. In contrast, the molds which frequently develop leave stains. *Aspergillus flavus* is the most dangerous followed by *A. niger*, *Penicillium frequentas*, and *Trichoderma viride*. With regard to the control of the organisms in plumping liquors, there are now a certain number of efficient commercial antifungal agents. The agents with a phenolic base are preferred to the quarternary ammonium salt base, since the latter precipitates the tannins. Since the strains adapt themselves to the antiseptic agents added, it is necessary to alternate the latter yearly. The alternation of two well chosen antifungal agents is sufficient. With regard to leather, it must be remembered that the antiseptics, in doses employed, do not kill the molds but stop their development. The leather removed from the plumping liquor will contain spores, and it will also pick up spores from the atmosphere of the tanneries. Under favorable conditions these molds will develop. It is, therefore, essential that the drying process be rapid, and that the leather be treated eventually with appropriate antifungal agents. R.H.

The Mechanical Properties of Chrome-tanned Collagen Fibers. F. Morgan. *J. Soc. Leather Trades Chemists*, **44**, 121–39 (1960).—This is the third in a series of papers in which the mechanical properties of untanned, vegetable-tanned, and chrome-tanned collagen fibers were examined (*JALCA*, **55**, 359,474). Variation in chrome-tanning procedure produced no significant changes in fiber strength and extensibility. Weight for weight, chrome-tanned fibers are about 25% weaker than raw fibers, the reduction of strength being nearly independent of chrome content of the fiber. Considerable variation in breaking load, breaking length, and breaking extension emphasizes the need for tests on many fibers and careful experimental control. J.M.C.

Chromatographic Fractionation of Acetic Acid–solubilized Rat Tail Tendon Collagen. A. Kessler, H. Rosen, and S. Levenson. *J. Biol. Chem.*, **235**, 989–94 (1960).—Gently heated soluble rat tail tendon collagen (homogeneous as judged by ultracentrifuge pattern) was chromatographed into at least four components by gradient elution chromatography on warmed (40°C.) carboxymethyl cellulose columns, under mild conditions of pH and low salt concentrations. Recovery of collagen from the columns was essentially complete. A forepeak (containing essentially low-molecular-weight products) and three incompletely separated components are consistent features of the chromatograms obtained. The forepeak obtained with an eluting acetic acid of less than 0.25*M* contained few amino acids and a low hydroxyproline content. J.M.C.

The Amino Acid Composition of Some Fish Collagens: The Relation between Composition and Structure. K. Piez and J. Gross. *J. Biol.*

Chem., **235**, 995–98 (1960).—The amino acid content (determined by ion exchange chromatography) of collagen from the scales, skin, and swim bladder of carp, from cod skin, and from pike skin is given. The role of imino acid pyrolidine rings in the intramolecular stability of collagen and the contribution of hydrogen bonding through hydroxylated amino acids to the intermolecular strength are stressed. J.M.C.

Structural Changes in Collagen. The Action of Alkalis and Acids in the Conversion of Collagen into Eucollagen. A. Courts. *Biochem J.*, **74**, 238–47 (1960).—N-terminal-residue assay is used to assess changes incurred in collagen (ossein) as a result of treatment with acid or alkali. Eucollagen is defined as collagen chemically modified so as to be transformed completely into gelatin (MW=60,000) in a few minutes in water below 60°C. Eucollagen in contrast to native adult collagen is readily soluble in dilute acid buffers. The principal N-terminal residue of bone collagen after demineralizing with acid is glycine, but amino groups of serine, threonine, aspartic, and glutamic acids appear after mild alkaline treatment. A preliminary soak of collagen in a strong cold acid accelerates the subsequent conversion into eucollagen with $Ca(OH)_2$ as much as 20-fold. The reverse order of these reagents is ineffective for this purpose. The bulk of the mucoprotein present in ossein does not appear to be a major factor in collagen stability. J.M.C.

Progress In Leather Science and Technology In India. Y. Nayudamma. *J. Soc. Leather Trades Chemists*, **44**, 113–21 (1960).—A review of the status of leather research and technology in India. J.M.C.

Synthetic Tannins and Their Importance for the Industry of Vegetable-tanned Leather in India. R. Bosse. *Tanner* (Bombay), **14**, 269–76 (1960).—An address. The development of syntans is outlined. Advantages of syntans include prevention of tannin loss through fermentation especially from myrobalans, improved color, shortened tanning time, and the possibility of using greater proportion of tanning materials that ordinarily have poor color or contain too much insoluble matter. H.B.M.

Hides and Skins. G. Douglas. *Tanner (Bombay). Annual No.*, **1960**, 25–27. **From Individuality to Association. Problems Facing the East India Tanning Industry.** R. Y. Gaitonde. *Ibid.*, 29–30. **Coordination between Government and the Leather Trade Associations.** S. Sankaran. *Ibid.*, 31–32. **The Future of India's Leather Trade.** M. George. *Ibid.*, 33–35. **Some Aspects of the Techniques of Retanning E.I. Leathers with Chrome.** P. S. Venkatachalam. *Ibid.*, 36–40. **Petroleum Products for the Leather Industry.** T. V. Jagadisan. *Ibid.*, 41–42. **Physics in Leather Technology.** N. Ramanathan. *Ibid.*, 43–46. **India and the Machines Age.** Anon. *Ibid.*, 49–50. **Germany—the Leading Country for Machinery for the Shoe and Leather Industry.** W. Frowein. *Ibid.*, 51–52. **Comments on Modern Tanning Industry.** C. Hall. *Ibid.*, 53–56. **Tannery and Shoemaking Machines of Czechoslovak Make.** R. Soukup. *Ibid.*, 57–60. **Machines from France.** Anon. *Ibid.*, 61–64. **Vulcanized Footware—A Story.** Anon. *Ibid.*, 65–68. **Mechanization in the Tannery.** H. S. Stebbing. *Ibid.*, 69–72. **Britain's Leather Industry: A 1959 Review.** M. George. *Ibid.*, 77–78. **The Leather Industry in Czechoslovakia.** F. Prochozka. *Ibid.*, 79. A series of brief reviews. H.B.M.

A New Hide Preservative: Paludrine. S. C. Nandy and S. N. Sen. *Bull. Central Leather Research Inst., Madras*, **6**, 315–28 (1960).—Paludrine (1-(*p*-chlorophenyl)-5-isopropyl-biguanide-HCl, an antimalarial agent, inhibited growth of bacteria from hides when 0.05% was added to the culture medium. Addition of 2% Paludrine to curing salt prevented development of red heat, while smaller amounts delayed the onset of red heat by several weeks. Treatment of hide with a solution of Paludrine containing 1% on the hide weight, in the absence of salt, for 10 hr., prevented the onset of hair slip and putrefaction for about a month and was much more effective than corresponding treatment with Na pentachlorophenate. Addition of 0.5% Paludrine, on the hide weight, to soak water prevented putrefaction for 4 days. Leather yield was not affected by use of 0.2% Paludrine in the soak water. H.B.M.

The Degree of Crystallinity of Collagen. S. Ghosh. *Bull. Central Leather Research Inst., Madras*, **6**, 331–33 (1960).—The linear thermal expansion coefficient of kangaroo tail tendon collagen, previously dried in vacuum over H_2SO_4 at 40°–50°C., was measured between room temperature and 90°C. and found to be 4×10^{-5}. By substituting this value in Flory's equations (*J. Am. Chem. Soc.*, **78**, 5222 [1956]), the degree of crystallinity was calculated to be 80%. This is in fair agreement with values calculated from the heat of melting of collagen and from the densities of collagen and gelatin. H.B.M.

Reappearance of Certain Structural Features of Native Collagen after Transformation. R. V. Rice. *Science*, **131**, 1319–20 (1960).—Electron micrographs of the particles present in calfskin collagen solutions were obtained before heating, immediately after heating, and after subjecting the solution to 5°C. for several hours. The characteristic rod-shaped collagen particles disappeared on heating and were replaced by globular particles; on cooling, the rod-shaped particles reappeared. The presence of highly ordered aggregates (segment long spacing type) was established after adding adenosine triphosphoric acid to heated and cooled collagen. Sedimentation, viscosity, and optical rotation studies confirmed these results. Electron microscope studies of collagen fibrils cross-linked with formalin revealed that the characteristic striations not only disappeared with elevation of temperature but also were regained on cooling. This study demonstrated that the reversal of the collagen helix⇆random coil transition is accomplished by restoration of the structure characteristic of the native state when proper heating and cooling schedules are followed. C.L.D.

Anomalies in the Microscopic Structure of Some Wools. T. D. Brown and W. J. Onions. *Nature*, **186**, 93–94 (1960).—On the basis of staining experiments with methylene blue it is demonstrated that in some fibers of some types of fine crossbred wools a core exists, usually at the junction between the ortho- and paracortex, which is more basophilic than the orthocortex. Staining with sodium plumbite indicates that this core is deficient in sulfur. It is proposed to call this core the metacortex. C.L.D.

Determining Covering Power for Leather of Dyes and Pigments. D. Kokes and K. Motycka. *Veda a vyzkum v prumyslu kozdelném*, **4**, 65–76 (1958); abstr. in *J. Soc. Dyers Colourists*, **76**, 261 (1960).—A 0.1% dispersion of the dye in casein is gradually added to a vessel through which light

passes from a stabilizer-fed 60-w bulb, filtered by ground glass, onto a photocell galvanometer unit. Volumes are compared at 20% decrease in transmission of light. There is an inverse exponential relationship between the concentration of dye and transmission of light above this value. In another test, which compared somewhat more favorably with tests on leather, glass disks were weighed, sprayed with a 5% to 15% dispersion of the dye, dried, and reweighed, and their light transmission was determined. C.L.D.

Aortic, Serum, Connective Tissue, and Osseous Chemistry in Lathyritic Rats. R. A. Grant, M. Hathorn, and T. Gillman. *Nature*, **186,** 164–65 (1960).—Rats suffering from *Lathyrus odoratus* intoxication have a possible increased cutaneous hydroxyproline content. It is suggested that the accumulation of mucopolysaccharide around the vascular elastic membranes of the lathyritic rat aorta may be due to some block in the neogenesis of their elastin and collagen-like fibrillar components, perhaps analogous to the block in collagen synthesis in healing wounds in scorbutic guinea pigs. C.L.D.

Collagenase Maceration of Kidney for Microdissection. Nancy Hayward. *Nature*, **186,** 403 (1960).—Kidney can be prepared for microdissection and subsequent nuclear staining by the use of the collagenase of *Clostridium histolyticum* for maceration of alcohol-acetic acid–fixed kidney. Formalin cannot be used because it alters the collagen substrate so that it is no longer susceptible to collagenase. Alcohol or acetone fixation does not inhibit the activity of collagenase. C.L.D.

Liberation of Hexuronic Acid, Hexosamine, and Hydroxyproline from Steerhide by Stem Bromelain. E. A. Botan and T. B. Brother. *Nature*, **186,** 314–15 (1960).—Hide squares from freshly flayed steerhide were soaked for 12 hr. at room temperature in a 4.5% saline solution with 0.1% sodium trichlorophenate; hexosamine, hexuronic acid, and hydroxyproline were then determined. The squares were then placed in a 1% bromelain solution (an enzyme mixture consisting primarily of plant proteases with limited amounts of phosphatases and amylase) with 0.1% trichlorophenate; the bromelain solution was maintained for 12 to 17 hr. at pH 6 to 6.8 and 30° to 35°C. Treatment of the hide with bromelain indicated a marked liberation of hexuronic acid (22.3%) and hexosamine (24.5%); hydroxyproline was released to the extent of 8.4%. The hair was loosened from the hair follicle and could be removed by applying a slight scraping action. Frozen sections of the unhaired hide stained with thionin showed complete removal of hair from the follicle, removal of the epidermis from the corium, and marked increased spacing between the clearly defined fiber bundles. C.L.D.

Report of the Commission on Leather Oiling Materials. R. Schubert, Chairman. *Das Leder*, **11,** 15–16 (1960).—Tentative methods are given for determining pH and charge of "water-soluble" oiling preparations. I.D.C.

Plastics and Their Base Materials as Tanning Substances. H. Batzer. *Leder Kurier*, **4,** 24–30 (1960).—A lecture reviewing the use of resins in monomeric or polymerized form for treating leather or tanning hides. I.D.C.

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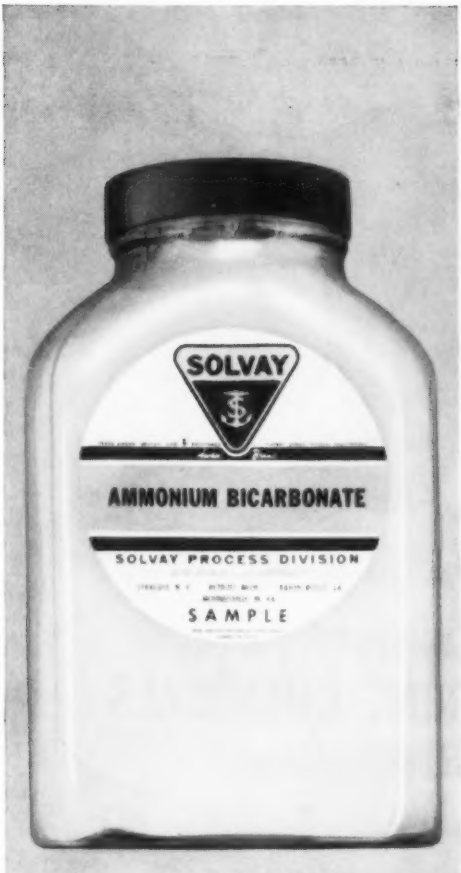

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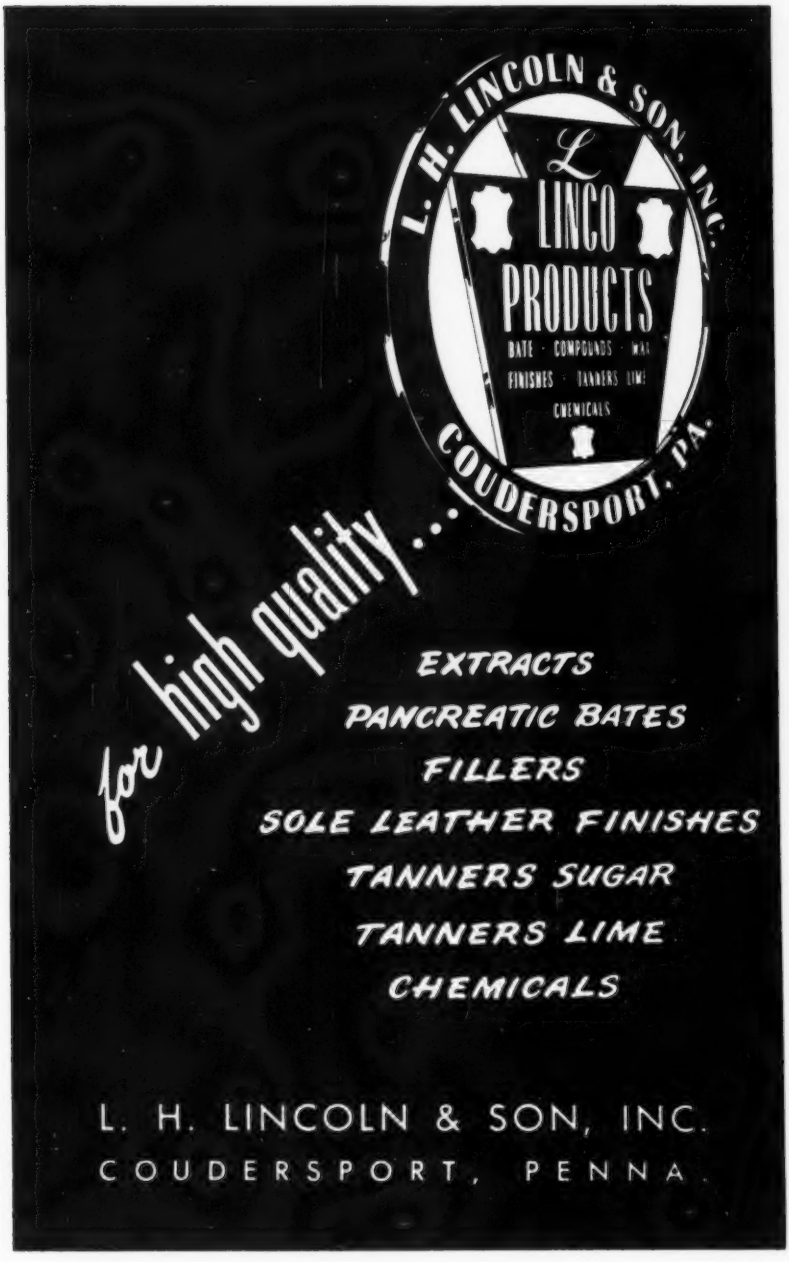
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"Z" AS IN ZEBRA

A side leather tanner told us this interesting process story recently. Troubled with a natural grease problem in his sides, he attempted to correct the situation by expensively solvent degreasing the stock early in the process.

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After such treatment the blue stock still oozed grease as it was laid on pallets. It was necessary to wring twice to obtain even passable splitting and he could not hold his weights on the splitting machine. Subsequent steps in the process were troublesome because of grease, and the finished sides were down-graded on the table.

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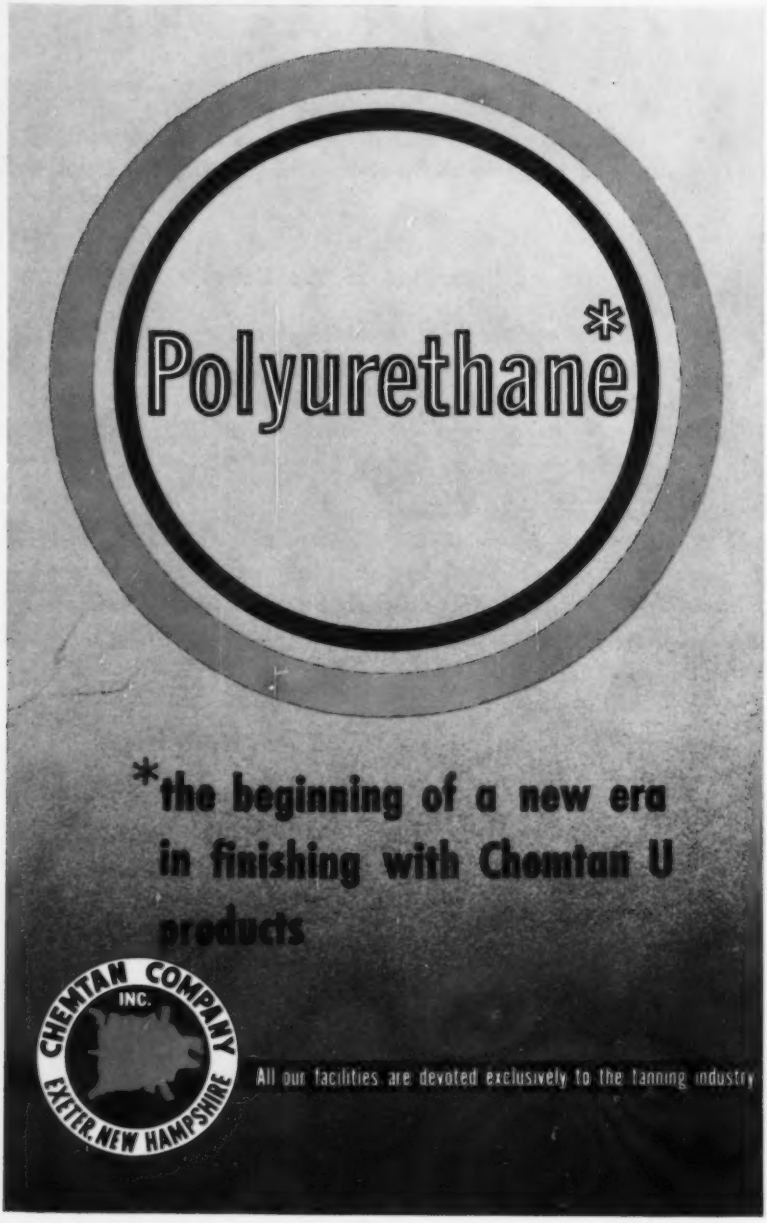
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